2010

Acid catalyzed carbohydrate degradation and dehydration

Basak Cinlar
Iowa State University

Follow this and additional works at: http://lib.dr.iastate.edu/etd
Part of the Biological Engineering Commons, and the Chemical Engineering Commons

Recommended Citation
Cinlar, Basak, 'Acid catalyzed carbohydrate degradation and dehydration' (2010). Graduate Theses and Dissertations. 11573.
http://lib.dr.iastate.edu/etd/11573

This Dissertation is brought to you for free and open access by the Graduate College at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Acid catalyzed carbohydrate degradation and dehydration

by

Basak Cinlar

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Brent H. Shanks, Major Professor
Andrew C. Hillier
Jay-lin Jane
Peter J. Reilly
Patricia Thiel

Iowa State University
Ames, Iowa
2010

Copyright © Basak Cinlar, 2010. All rights reserved.
To my grandparents, Mucella and Ali Bayram…
# TABLE OF CONTENTS

ACKNOWLEDGMENTS .......................................................................................................................................... v

ABSTRACT .......................................................................................................................................................... vi

CHAPTER 1. INTRODUCTION AND LITERATURE REVIEW ................................................................. 1
  Dissertation Organization ................................................................................................................................. 2
  Overview of Mesoporous Silica as Catalysts ................................................................................................. 4
  Overview of Dehydration Reaction Studies ................................................................................................. 11
  References ....................................................................................................................................................... 16

CHAPTER 2. CHARACTERIZATION OF CATALYTIC SITES IN ORGANIC ACID FUNCTIONALIZED MESOPOROUS SILICA IN AQUEOUS MEDIA ................................... 19
  Abstract .......................................................................................................................................................... 19
  Introduction .................................................................................................................................................. 19
  Experimental ............................................................................................................................................... 23
  Results and Discussions ............................................................................................................................... 26
  Conclusions .................................................................................................................................................. 43
  References ....................................................................................................................................................... 44

CHAPTER 3. QUANTUM CHEMICAL MODELING OF SOLVATION OF ORGANIC ACID FUNCTIONALIZED GROUP IN MESOPOROUS SILICA ........................................ 47
  Abstract .......................................................................................................................................................... 47
  Introduction .................................................................................................................................................. 48
  Computational Methods ............................................................................................................................... 51
  Results and Discussions ............................................................................................................................... 52
  Conclusions .................................................................................................................................................. 61
  References ....................................................................................................................................................... 61

CHAPTER 4. KINETICS OF MONOSACCHARIDE CONVERSION IN THE PRESENCE OF HOMOGENEOUS ACIDS ............................................................................ 63
  Abstract .......................................................................................................................................................... 63
  Introduction .................................................................................................................................................. 64
  Experimental ............................................................................................................................................... 69
  Results and Discussions ............................................................................................................................... 71
  Conclusions .................................................................................................................................................. 86
  References ....................................................................................................................................................... 87
<table>
<thead>
<tr>
<th>CHAPTER 5. HIGHLY EFFICIENT HYDROXYMETHYL FURFURAL PRODUCTION FROM GLUCOSE</th>
<th>89</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>89</td>
</tr>
<tr>
<td>Introduction</td>
<td>90</td>
</tr>
<tr>
<td>Experimental</td>
<td>93</td>
</tr>
<tr>
<td>Results and Discussions</td>
<td>95</td>
</tr>
<tr>
<td>Conclusions</td>
<td>109</td>
</tr>
<tr>
<td>References</td>
<td>109</td>
</tr>
</tbody>
</table>

| CHAPTER 6. FUTURE CONSIDERATIONS AND GENERAL CONCLUSIONS | 112 |

<table>
<thead>
<tr>
<th>APPENDIX 1. MONOSACCHARIDE DEHYDRATION USING ORGANIC-INORGANIC HYBRID MESOPOROUS SILICA</th>
<th>118</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>118</td>
</tr>
<tr>
<td>Introduction</td>
<td>119</td>
</tr>
<tr>
<td>Experimental</td>
<td>121</td>
</tr>
<tr>
<td>Results and Discussions</td>
<td>124</td>
</tr>
<tr>
<td>Conclusions</td>
<td>133</td>
</tr>
<tr>
<td>References</td>
<td>133</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>APPENDIX 2. SULFATED ZIRCONIA MODIFIED SBA-15 CATALYSTS FOR CELLOBIOSE HYDROLYSIS</th>
<th>136</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>136</td>
</tr>
<tr>
<td>Introduction</td>
<td>137</td>
</tr>
<tr>
<td>Experimental</td>
<td>139</td>
</tr>
<tr>
<td>Results and Discussions</td>
<td>142</td>
</tr>
<tr>
<td>Conclusions</td>
<td>155</td>
</tr>
<tr>
<td>References</td>
<td>155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>APPENDIX 3. STUDY ON THE HYDROTHERMAL STABILITY OF SULFATED ZIRCONIUM MODIFIED SBA-15</th>
<th>158</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>158</td>
</tr>
<tr>
<td>Introduction</td>
<td>159</td>
</tr>
<tr>
<td>Experimental</td>
<td>161</td>
</tr>
<tr>
<td>Results and Discussions</td>
<td>164</td>
</tr>
<tr>
<td>Conclusions</td>
<td>176</td>
</tr>
<tr>
<td>References</td>
<td>176</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

I am heartily thankful to my major professor Brent H. Shanks, whose encouragement, supervision and support made this thesis possible. Moreover, I would like to thank him for his guidance that broadened my vision and helped me to develop my own perspective. I also would like to thank to James A. Dumesic and Yomaira Pagan-Torres from University of Wisconsin-Madison, Emiel Hensen and Volkan Degirmenci from Technical University of Eindhoven, the Netherlands, and Haiyang Zhu from my research group for their invaluable collaborations; and I would like to present my appreciation to Mark S. Gordon for his support and contributions at each level of my computational studies. I owe my sincere gratitude to Deniz Uner, whose wisdom, knowledge and commitment inspired me throughout my entire studies.

All my group members, especially Sikander Hakim and Sarah L.Hruby, deserve many thanks for their helpful discussion and comments, which added significant value to my work. I would like to thank also to the undergraduate students that helped me in this work, Brandon Peters, Elliot Combs, Miriam Garcia-Fierro and Cody Jensen.

Writing this thesis has been one of the most significant challenges in my life. I cannot express my thankfulness enough to my friends and family members who have endured me through this period. I would like to especially thank to Can Ozer, and Arzu Alici. Most importantly, I owe my greatest appreciation to my family; Seda, Isik and Orhan Cinlar, for their continuous support.
ABSTRACT

Facile commercial production of versatile polyfunctional compounds from biomass constitutes a great challenge in establishing a sustainable chemical industry. One such example is the production of furfural and hydroxymethyl furfural (HMF) via dehydration of pentoses and hexoses, respectively. These chemicals are of great interest as primary building blocks in the polymer industry. However, their large scale production is hindered due to several problems, such as feedstock availability, low product yields due to excessive side reactions and lack of an industrially feasible heterogeneous catalyst.

Organic acid functional groups incorporated onto mesoporous silica offer well defined catalytic sites in addition to the unique textural properties and thus give the material the potential to be a promising catalyst. However, a rational approach for fine tuning of the catalyst properties to meet the reaction system requirements entails detailed understanding of the nature of the catalytic sites in condensed phase under the conditions that mimic the reaction environment. Towards that aim, the current work presents a methodology for the characterization in condensed phase, using potentiometric titrations. Procedures for accurately determining the acidic strength and total acid capacity of the organic acid functionalized materials are presented. The results revealed that organic acid moieties of different strength display their characteristic acidity without being leveled in water. The strongest acid was the arene sulfonic group followed by propyl sulfonic, ethyl phosphonic and butyl carboxylic.

The results obtained for propyl sulfonic and arene sulfonic groups were not in complete agreement with literature. The discrepancy could be attributed to the fact that most of these previous studies had examined the interaction of the acidic group with a
gas phase probe molecule, while the effect of solvation was neglected. In the present work, the effect of solvation on the acidic strength of these moieties was investigated via quantum chemical simulations. A change in the acidic strength trend was observed with the increasing number of water molecules, indicating that one-to-one interaction in the gas phase does not necessarily represent the interaction of the moiety with the solvent molecules.

The difference in the acidic strength for these organic acid groups incorporated onto mesoporous silica was not observed when they were tested for their activity on hexose and pentose dehydration due to poor hydrothermal stability of the materials at elevated temperatures. Sulfated zirconia doped mesoporous silica materials, which displayed high activity in cellobiose hydrolysis, did not provide desired hydrothermal stability either for dehydration reactions. Further research is focused on developing a hydrothermally stable catalyst for condensed phase reactions.

Although a lot of study has focused on monosaccharide decomposition, the information available in literature is highly unorganized and does not provide the insight about the catalytic properties or process conditions required for high yields. The current work presents a systematic study with homogeneous mineral and organic acids of varying strength to build a platform for catalyst comparison. The study revealed that depending on the pH of the solution, different mechanisms underlie the glucose decomposition in the presence of weak acids. Although lower acid concentration leads to higher selectivity toward HMF, this could not be considered as an industrially viable solution.

While attempting to develop an industrially feasible process to obtain high yield of HMF from glucose, it was discovered that addition of alkaline earth metals and application of pressure in the presence of acid catalyst activates the glucose ring
resulting in high HMF yields. Further enhancement was obtained by addition of an organic phase for HMF extraction. This unprecedented process can be combined with polysaccharides hydrolysis and one pot HMF production from biomass. By further optimization of the parameters, an industrially feasible process for HMF production can be achieved.

Thus current work is very significant and relevant in providing perceptions for developing an industrially feasible process with heterogeneous acid catalysts to produce furanic compounds from biomass.
Chapter 1. INTRODUCTION AND LITERATURE REVIEW

The interest for a non-petroleum based industry has been increasing in the hope of improving the environmental quality; maintaining national security, using the excess agricultural production and supporting the rural development [1]. For a non-petroleum based economy, biomass derived materials need to be involved in transportation, fuel, fibers and the chemical industry [1]. Among bio-based chemicals, furanic compounds play a key role in the production of higher alkane liquid fuels for transportation purposes and in the production of wide-range of other important chemicals in the polymer industry [2, 3]. Furanic compounds are produced from biomass rich in carbohydrates. The method consists of hydrolysis of polysaccharides into monosaccharides followed by their dehydration [3]. While furfural is obtained from pentoses such as xylose, arabinose and ribose, six-carbon sugars such as fructose and glucose lead to 5-hydroxy-2-methylfurfural (HMF).

For the industrial production of furfural, concentrated sulfuric acid is employed using Quaker Oats technology [2]. However, its corrosivity and toxicity add to the other drawbacks such as high separation and recycling cost of homogeneous acids. For the industrial production of HMF, fructose is used as feedstock currently, but its lower abundance increases the production cost and thereby hinders production in massive scales. Although glucose is a more preferred feedstock due to its higher abundance, there is no cost-effective process using glucose developed yet due to its stable structure [3-5]. As a result, for industrial production of both furfural and HMF, developing an environment-friendly heterogeneous catalyst with high yields is essential [3-6]. This project aimed to provide guidance about the design of an industrially feasible process
with an environment friendly heterogeneous catalyst for the dehydration of monosaccharides.

**Dissertation Organization**

Organic acid functionalized mesoporous silicas offering high surface area with tunable textural and catalytic properties were considered as promising catalysts for the dehydration of monosaccharides. These materials have attracted great interest as catalysts in several reactions from many areas including the hydrolysis of oligosaccharides into monosaccharides. In fact the dehydration products, hydroxymethylfurfural and furfural, were already recognized among the products during the hydrolysis of oligosaccharides. With the ability of further tuning the catalytic properties of these catalysts, organic acid functionalized mesoporous silica catalysts promised potential.

A methodological approach in tailoring the catalytic properties for monosaccharide dehydration necessitated understanding the catalytic features of these materials in condensed phase. Most of the previous studies have been focused on characterization of the acidic features based on their interaction with a gas phase probe molecule and excluded the effects of solvation on acidic features. For the determination of acidic strength and total acid capacity of organic acid functionalized mesoporous silica in condensed phase, a detailed characterization method using potentiometric titration is developed in Chapter 2. For further investigation of the role of solvation on the acidic strength for these materials, the functional groups attached on model silica supports were simulated ab initio in the presence of water molecules in Chapter 3.

Dehydration of monosaccharides has been an attractive issue for scientists for a long time. Since C-C and C-O bond breakages have similar activation energies, many other
side reactions accompany dehydration which complicates the reaction system, and prevents to gain insight and understanding the mechanisms. Only few studies reported systematic data about the catalytic features, whether it is a homogenous or a heterogeneous. In Chapter 4, mineral and organic homogeneous acids of varying strength were evaluated for their activity towards monosaccharide decomposition in attempt to build a common framework for catalyst activity comparison. In Chapter 5, in collaboration with University of Wisconsin-Madison, a method is proposed for the dehydration of glucose with high yields that allows also combining polysaccharide hydrolysis with the dehydration. By further optimization of the reaction parameters and substitution of the homogenous catalyst with a heterogeneous catalyst, the proposed method is potentially commercializable.

The activity of organic acid functionalized mesoporous silica materials was tested for the dehydration of pentoses and hexoses in Appendix 1. The results indicated that hydrothermal stability problems arose at the reaction conditions for dehydration reaction. Because sulfated zirconia doping on mesoporous silica was proposed to improve the hydrothermal stability, these materials were investigated for their catalytic properties and for their activity towards cellobiose hydrolysis in a joint project with Middle East Technical University and Technical University of Eindhoven and is presented in Appendix 2. Appendix 3 addresses the hydrothermal stability problems that also arose for sulfated zirconia doped mesoporous silica.

A study performed by another group member showed that changing the catalyst support from silica to activated carbon increased hydrothermal stability problem and making sulfonated activated carbon catalysts hydrothermally stable at the conditions used for dehydration reaction. In fact the catalyst showed comparable activity to sulfuric acid for fructose dehydration. By further improvement of the catalytic and textural
properties, the sulfonated activated carbon catalyst is a promising catalyst for the process developed in Chapter 5 for glucose dehydration.

**Overview of Functionalized Mesoporous Silica as Catalysts**

Since their discovery by Mobil Co. in 1992 [7], functionalized mesoporous silica catalysts have been used for various reaction systems because of their tunable textural and catalytic properties. Some of these reactions include Michael additions [8], Knoevenagel reactions [9-11], esterification [12-14], and polysaccharide hydrolysis [15, 16]. According to the reaction system under interest, mesoporous silica structures are tailored by choosing the type of silica support, functional group and the method for functionalization.

Mesoporous silica supports are synthesized using a micelle-template [7]. The silica structure self-assembles around the template by hydrolysis and condensation of the silica precursor, tetraethoxysilane or tetramethoxysilane. After the formation of the silica structure the surfactant is removed either by solvent extraction or by calcination. In Figure 1, the self-assembly process of silica support around the micelle template is shown [17]. Depending on the synthesis method and the type of surfactant used for micelle formation, mesoporous silica structures can be hexagonal, cubic, or lamellar [18]. Moreover, there are different types of surfactants used for synthesis of hexagonally ordered mesoporous silica to tailor the pore size and wall thickness.
The first synthesized mesoporous materials were MCM-41 using a quartenary ammonium surfactant under basic conditions [7]. Removal of the surfactant requires acid extraction or calcination. The extreme conditions for the surfactant removal does not allow simultaneous introduction of functional groups during the silica support synthesis. Functional groups are grafted after the template removal. Functionalization of MCM-41 structure using this method was first reported by Burkett et al. in 1996 [19].

HMS silicas, first reported by Tanev and Pinnavaia in 1994 [20], are templated using a neutral surfactant, such as dodecylamine. The pore size can be adjusted by the choice of surfactant; hence the longer the aliphatic chain is, the larger the pores will be. Surfactant removal is easier than for MCM-41, and can be done by ethanol extraction. The resulting HMS structure is a spongelike structure with wormhole-like pores and has thicker walls than MCM-41 [19, 21]. However, the MCM-41 type displays improved long-range order compared to HMS.

SBA-15, first reported by Zhao et al. in 1998 [22], is assembled under acidic conditions using a tri-block copolymer consisting of polyethylenoxide (PE) - polypropylene (PO) -polyethylenoxide (PE). Micelle formation occurs due to the highly hydrophilic character of EO blocks and the partially hydrophilic character of PO blocks. While the micelle core is formed by PO blocks, the EO blocks remain at the
interface interacting with the solvent and silica precursor via hydrogen-bonding [17]. The extension PO blocks into the silica network cause SBA-15 have a micropore network too. The size of the micropores is 5-15Å, whereas the size of mesopores can go up to 300Å. The lengths of the polymer blocks are responsible for the pore size, but the pore size can also be adjusted by varying the temperature during synthesis or aging. The increasing temperature leads to smaller pore sizes due to decreased solubility of EO blocks. Once the surfactant is removed by ethanol extraction, the resulting SBA-15 structure has a wall thickness of 31-64Å that is thicker than those for HMS and MCM-41. The larger wall thickness provides higher thermal stability to SBA-15 compared to MCM-41 and HMS [18]. The wall-structure of these hexagonally ordered mesoporous silica structures can further be modified by introduction of polymers or short alkyl chains to add hydrophobic or hydrophilic character to the support [23].

The surface properties can be also tuned by thermal treatment. Thermal treatment leads to condensation of surface silanols to form siloxane bonds making the surface less hydrophilic [24, 25]. Density and type of surface silanols and the spacing between them is determined by the pore curvature. There are three types of silanols present in mesoporous silica structure: isolated, geminal, and hydrogen-bonded. The distribution of these different silanol types on the surface defines the acidic strength of the support. Silanols can act as Bronsted acids, hydrogen bond donors or hydrogen bond acceptors [26]. The $pK_a$ for hydrogen bonded silanols was reported to be as low as 4.5, due to share of proton between two silanols leaving the proton from one silanol group relatively free [27]. Recently, a study on SBA-15 surface with adsorption of benzylamine proposed that the $pK_a$ for the acidic silanols is even lower than 4.5, that is equal or less than 2 [28]. The $pK_a$ for geminal silanols was reported to be 8.5 or 8.2 [27, 28], significantly less acidic than hydrogen-bonded silanols.
Catalytic activity of these materials is achieved by incorporation of functional groups that involve an alkoxy silicone with functional group moieties reacting with surface silanols to anchor the functional group onto the surface. The incorporation can be performed simultaneously during the formation of the silica support via co-condensation or after the removal of the surfactant via grafting. Multiple groups can be introduced at the same time or sequentially by grafting of one group following co-condensation of the other. The choice of incorporation method affects the distribution and density of the functional groups, hence influencing the catalytic activity of the resulting material.

Grafting, the post synthesis method after template removal, is performed mostly in a non-polar solvent in order to facilitate the anchoring of the functional group precursor to the surface silanols. Still, mass transfer issues take place, and the functional groups tend to accumulate at the pore openings or at the exterior of the material, which was shown by Lim and Stein [29] when studying dispersion of vinyl groups on MCM-41 structure. On the other hand, infrared studies on SBA-15 with butyl carboxylic groups [30] demonstrated that functional groups incorporated via co-condensation during the silica support formation mostly reside within the pores more uniformly distributed than grafted groups. Also Mbaraka and Shanks[14] confirmed the results when they incorporated hydrophobic alkyl groups onto SBA-15 surface via co-condensation and grafting. When grafted, the alkyl groups rendered the materials hydrophobic while the hydrophilicity was retained with the co-condensed groups. Distribution of functional groups via grafting and co-condensation is shown in Figure 2.
Figure 2. Distribution of hydrophobic groups (RICS) onto mesoporous silica with co-condensed functional (Z groups; a) via grafting, b) via co-condensation [14]

The loading density is also affected by the incorporation method. Grafting allows high loadings, almost up to full surface coverage; whereas co-condensing more than 40 mole % distracts the structural order [31]. Typical loading ratio for co-condensation ranges between 5-15 %. When grafted, the actual loading on the silica surface depends on the surface silanol density that cannot be controlled. During grafting, deposition of the functional groups at the pore mouth narrows the pore size and thereby promotes accumulation at the pore entrance further due to increased mass transfer limitations. Another drawback of grafting appears if the surfactant is removed by calcination. Calcination causes dehydroxylation of the surface locally, and those areas tend to host clusters of functional groups during grafting. Furthermore; when grafted, the functional groups may not condense with hydroxyl groups completely, which reduces the stability of the functional groups [17, 18, 23]. As a result, co-condensation allows for less loading of functional groups but provides a better control on them as compared to grafting.

Neither grafting nor co-condensation provides control on spacing between the functional groups. Controlled spacing of the functional groups can be achieved via imprinting. The method is first developed by Katz et al. [32] for the silica gel. In this
method, an organic scaffold containing the functional groups is incorporated into the silica support during sol-gel synthesis. After the removal of the scaffold, functional groups remain at the spaces with controlled distances. However, this method has not been applied to mesoporous silica materials leaving grafting and co-condensation as the most widely used techniques.

Using grafting or co-condensation, a wide variety of functional groups, acids and bases as well as hydrophobic and hydrophilic groups, has been incorporated onto mesoporous silica support. Acid groups may not be added directly to the media, as they would interfere with the self-assembly process of silica around micelle-template. A prehydrolysis period for formation of silica support must be allowed before addition of the organic acid precursors into the synthesis media [18]. Among the organic acids, the most commonly co-condensed groups are propyl sulfonic and arenesulfonic groups [33, 34]. For the incorporation of propylsulfonic groups, an alkoxy silane precursor with thiol groups is used, where thiol groups are oxidized to sulfonic acid groups using hydrogen peroxide. The sulfonic acid groups are formed in the acidic media during the synthesis of the silica support and do not require further modification. Also weaker organic acids, such as ethyl phosphonic acid [35] and butyl carboxylic acid [36] are co-condensed. As butyl carboxylic group precursor, cyanoethyl or cyanopropyl groups are used, which are hydrolyzed in the acidic media during the synthesis. The alkoxy silane precursor structures for these functional groups are shown in Figure 3.
Among organic bases, the propylamine group is the most commonly co-condensed functional group [10, 11, 37, 38]. Aminopropyltriethoxysilane is used as precursor and no further modification is required. Amine groups are protonated automatically under the acidic conditions for SBA-15 formation. Beside propylamine, diamines [39], imidazole [40], dihydroimidazole [41], and pyridine derivatives [42] are also incorporated onto the SBA-15 surface. The effect of the base groups can be shielded by their interaction with the surface silanols. To prevent this, surface silanols are capped with hexamethyldisilazane [43] or a tritylimine patterning agent [44] is used.

The hydrophilic character of the surface can be adjusted by incorporation of hydrophobic or neutral groups such as ethyl, methyl or phenyl groups [14]. This is mostly used to shift the reaction selectivity towards non-polar reactants. There is also some work about incorporating chiral groups for enantioselective reactions [45, 46] and ionic liquid immobilization to reduce the separation cost from reaction media [47].
methyl-3-propylimidazolium and 1-propylpyridinium ionic liquids are among those incorporated ionic liquids onto SBA-15.

**Overview of Dehydration Reaction Studies**

Furanic compounds are produced from biomass by monosaccharide dehydration following polysaccharide hydrolysis and they serve as essential intermediates in the production of liquid alkanes [3]. Previously a process converting sugar alcohols into light alkane (C1-C6) products has been developed [3]. However due to their high volatility, light alkanes cannot be used for fuel applications. On the other hand, liquid alkanes that can be produced from biomass-derived carbohydrates provide a renewable source for transportation fuel. Conversion of biomass-derived carbohydrates into liquid alkanes involves several sequential reactions, where dehydration reactions play a key role [3]. The overall scheme to produce liquid alkanes from furanic compounds is shown in Scheme 1.

Scheme 1. Reaction pathways for conversion of saccharides into liquid alkanes [3].
During the dehydration reaction of both pentoses and hexoses, the reaction intermediates and the products can degrade further to various by-products via fragmentation, condensation, rehydration, reversion and/or additional dehydration reactions [48]. Scheme 2 summarizes the side reactions taking place during dehydration and the common side products.

Scheme 2: Monosaccharide degradation pathways [49-51].

Mechanistic studies to explain the formation of furfural and other by-products have been conducted on the pathway of xylose to furfural as well as fructose to HMF dehydration. According to Dunlop and Root [52], the xylose disappearance is first order and proportional to the initial acid concentration. Furthermore, a prior intermediate of unknown identity was responsible for furfural formation. Antal in 1991 [50] identified this as the 2, 5 anhydride intermediate, and it is the main channel that forms 2-furaldehydes from aldoses. Another mechanistic study [51] indicated the presence of intramolecular etherification reactions. However, Defaye [53] concluded the etherification reactions play only a minor role and the dehydration takes place mainly via 2,5-anhydro sugars. In 1991, Antal et al. [50] showed that at 250°C in the presence of 0.001-0.02M sulfuric acid the open chain isomer is initially present and quickly
reacts to form glyceraldehyde, pyruvaldehyde, lactic acid, glycolaldehyde, formic acid, lyxose and arabinose. The furanose ring form is present in small amounts and is relatively stable, whereas the pyranose ring form leads to furfural via 2, 5 anhydrides. Indeed without any catalyst, furfural formation rate accelerated for short residence times due to the autocatalytic mechanism. The proposed mechanism for xylose dehydration is shown in Figure 4.

![Dehydration mechanism of xylose](image)

**Figure 4.** Dehydration mechanism of xylose [2].

As using homogeneous mineral acids are not environmentally friendly and add to the cost by separation and recycling issues, several attempts have been made to employ heterogeneous catalysts for the dehydration reaction. Heterogeneous catalysts such as strong acid cation exchange resins [5], H-form zeolites [54-56] as well as niobium, titanium, zirconium, and vanadyl phosphates [48, 57-59] have been proposed to catalyze dehydration of monosaccharides. H-form zeolites have recently shown promising
results. Moreau et al. [55] reported that the only one large channel bidimensional structured H-mordenites is more selective and but also less active than three-dimensional H-Y faujasites with 13Å cavities inside at 170˚C on the dehydration reaction of xylose. The highest selectivity achieved was about 96-90% in 30-50 min for xylose conversion of 27-37% in water/toluene mixture at 170˚C on H-mordenites. Similar selectivity (90%) but better conversion rates (54-76%) were obtained for the dehydration of fructose to 5-hydroxymethylfurfural at 165˚C in water/methylisobutylketone mixture on H-form mordenites [56].

Niobium, zirconium and titanium catalysts attenuated levulinic and formic acid formation that constitutes a problem when aqueous media is used [48, 58, 59]. Moreover the improved selectivity when niobium phosphates are used has been attributed to higher strength of Lewis and Bronsted acid sites [48]. Also, studies on heterogeneous vanadyl phosphate derivatives characterized by a stronger Lewis acidity with respect to vanadyl phosphate itself showed an improved catalytic activity on dehydration of fructose [59]. The selectivity enhancement effect of Lewis acid sites has also been proven on heterogeneous titanium and zirconium based catalysts [58]. Also, differently supported catalysts showing comparable activity showed different selectivity indicating the importance of the nature of the support.

Although the traditional heterogeneous catalysts have shown promising results, their low surface area limits their usage. Their alternatives are the traditional heterogeneous catalysts are organic-inorganic hybrid silicas which involves incorporation of organic groups on mesoporous silica supports. Due to their high surface areas and their flexible pore size they found a wide application area. Dehydration of xylose into furfural has been studied over MCM-41 type catalysts functionalized with sulfonic acid [60]. The best selectivity achieved was 82% for a conversion of 91% for sulfonic acid coated
MCM-41 at 140°C. In this study, contrary to others, the selectivity increased with increasing conversion. Still, it has been concluded that the selectivity can be further improved by fine-tuning of the median pore size. In order to prevent furfural degrading further, a biphasic system of isobutylmethylketone (IBMK)/water was used where furfural was continuously extracted into IBMK phase. Also, some other works [5, 48] have shown that the biphasic systems, designed to extract furfural either by IBMK or toluene, lead to improved selectivities. A biphasic system consisting of aqueous reactor phase modified with DMSO and/or poly (1-vinyl-2-pyrrolidinone) and extracting organic phase with IBMK and 2-butanol resulted in 85% selectivity for 89% fructose conversion using hydrochloric acid as catalyst [61]. The reason of adding phase-modifiers was explained by suppressing side reactions and enhancing the extractive properties.

Another study with mesoporous silica supported 12-tungstophosphoric acid for dehydration of xylose [62] followed the work with sulfonic acid functionalized MCM-41, but these are the only studies with mesoporous silica catalysts. The activity of organic acid functionalized SBA-15 for dehydration reaction has not been investigated. However these materials were active for cellobiose hydrolysis [16], a reaction system with similar kinetics to the dehydration reaction. The studies on cellobiose hydrolysis revealed that the proton concentration was the only factor affecting the kinetics, but the acidic strength of the functional group had no effect. If organic acid functionalized SBA-15 are to be tested for dehydration reaction, first this phenomenon has to be explained with a deeper understanding about the nature of the catalytic sites. The second problem is the lack of systematic data in literature to compare catalytic activities. This platform must be built via systematic study with homogeneous acids to compare the relative activities and outline the important parameters about the reaction.
References


CHAPTER 2. CHARACTERIZATION OF CATALYTIC SITES IN ORGANIC ACID FUNCTIONALIZED MESOPOROUS SILICA IN AQUEOUS MEDIA

A paper submitted to Journal of Catalysis

Basak Cinlar and Brent H. Shanks

Abstract

Exploring the catalytic potential of organic acid functionalized mesoporous silica in condensed phase necessitates characterization of their acidic properties in a similar environment. In this study, potentiometric titration is used as a direct measurement technique to determine the acidic strength and total acid capacity of propyl sulfonic, arene sulfonic, ethyl phosphonic, and butyl carboxylic functionalized mesoporous silica catalysts in water. While the method can provide direct insight into the acidic properties of the materials, the characterization conditions must be carefully chosen to yield reliable results. The addition of salts are required for enhancing the ion-exchange in the titration procedure, but their over-addition results in deviation of the activity coefficients leading to incorrect results. Titrations, performed under reliable characterization conditions, demonstrate that network interactions can exist between the organic acid functional groups. While the strongest acidity is observed for the arene sulfonic acid functionalized material, none of the acidic materials are leveled in an aqueous solvent.

Introduction

Due to their well-defined catalytic sites combined with tunable textural properties, organic acid functionalized mesoporous silica materials have been evaluated as catalysts for numerous condensed phase reactions [1, 2]. Aqueous phase reactions such as
cellulbiose hydrolysis [3] and monosaccharide dehydration [4] have also been reported. Improved yields for these aqueous phase reactions, both of which are potentially important for a bio-based industry [5], rely on better understanding of the acidic sites in the condensed phase reaction environment. Previous characterization studies [6-13] provide limited information, because acidic strength was primarily determined based on adsorption characteristics of only a probe molecule thereby disregarding solvation effects. In the few studies in which organic acid functionalized mesoporous silica were characterized in solution [3, 14-21], a systematic approach was not utilized to evaluate acid groups of varying strength and the effect of the characterization conditions on the results was not sufficiently controlled. In the current study, the properties of organic acids of varying strength tethered onto mesoporous silica were investigated via potentiometric titration, which allows for direct measurement of acidic properties in solution. Additionally, the effect of the characterization conditions was addressed by estimating solution activity coefficients.

The strength of an organic acid tethered onto a substrate is dictated not only by the chemical composition of the acidic moiety, but also by its concentration on the support and its interaction with the surface [15, 18, 20, 22, 23]. For example, in previous studies the acidic strength of sulfonic acid groups, attached onto SBA-15 surface, that were in close proximity from use of a disulfide precursor were found to be higher than for more isolated sulfonic acid groups [15, 23]. It was shown that the controlled spacing between the functional groups altered their acidic strength. Additionally, the interaction of the silica backbone with the functional groups may affect the acidic strength of the tethered groups. The pore curvature varies for silica supports having different pore diameters and hence the density, type of surface silanols and the spacing between them vary, which may affect the strength of interaction with the functional groups [24, 25]. There
are three types of silanols present in the mesoporous silica structure: isolated, geminal, and hydrogen-bonded, which can act as Brönsted acids, hydrogen bond donors or hydrogen bond acceptors depending on their density and spacing. The reported $pK_a$ values for different silanols vary from 4.5 (for hydrogen bonded) to 8.5 (for geminal) [26]. Silanols with different acid strengths will interact differently with functional groups and as a result might change the overall measured acid strength of a material.

A plethora of techniques including temperature programmed desorption (TPD), in situ FT-IR and 2-D solid-state NMR have been used with probe molecules such as carbon monoxide, ammonia, triethylphosphine oxide (TEPO) and pyridine to characterize propyl sulfonic (-PrSO$_3$H), ethyl phosphoric (-EtPO$_3$H), butyl carboxylic (-BuCOOH) and arena sulfonic (-ArSO$_3$H) functional groups tethered on silica surfaces [6-10, 13]. According to TPD studies with pyridine, the acidic strengths of -PrSO$_3$H and -ArSO$_3$H were found to be close to each other, with -PrSO$_3$H being reported as slightly more acidic [27]. However, the $^{31}$P- MAS NMR studies with TEPO suggested -ArSO$_3$H to be the stronger acidic group [10]. This discrepancy can further be extended to other studies, where the trends among the functional groups showed differences according to the method and/or the probe molecule used. Moreover, these techniques estimate the acidic strength of a functional group based on the interaction with probe molecules in the gas phase and do not account for solvent effects. Alternatively, the reaction of phenol and bisphenol A was used to compare the activities of different functional groups with an inferred relationship between activity and acid strength [23]. However, the concern with using catalytic activity to infer acidic strength is the potential to convolute mass transfer effects with kinetics. Even if the effects are successfully deconvoluted, the results are potentially solvent specific as the nature of the solvent can affect the acidic strength of the catalytic sites. For example, in a study
comparing the acid strength of sulfonated polystyrene resin and sulfonated mesoporous silica in aqueous and non-aqueous media [28], the molar enthalpies of neutralization suggested that the polystyrene supported catalysts were more acidic than the mesoporous catalysts in water, but the trend was reversed in the non-aqueous systems. Overall, the acidic strengths determined by calorimetric desorption studies, spectroscopic methods or kinetic studies must be carefully related to their strengths in the condensed phase as the solvent employed can affect the acidic properties significantly.

Potentiometric titration allows for direct determination of acidic strength and total acid capacity in solutions, but it has its own limitations requiring the experimental conditions to be carefully selected. In titrating homogeneous acids, the enthalpy of neutralization depends on proton loss from the acid, proton gain by the corresponding base, and changes in the solvation due to formation of conjugate pairs [28]. In the case of heterogeneous acid titrations, mass transfer issues can also become important [29]. Thus, the titration conditions must be carefully controlled to assure equilibrium between each injection of the titrating species in the characterization of organic acid functionalized mesoporous silica. Additionally, as the ion concentration is increased the measured proton activity may differ from the actual proton concentration as the solution activity coefficient deviates from unity. This effect is important as salts are typically added to the titration media in order to facilitate the ion-exchange and accelerate the electrode response [30]. Either high concentrations of the salt or the solute can cause the activity coefficient to deviate significantly from ideality.

In addition to these limitations, there are some important properties of water that must be considered when investigating acidic properties in an aqueous media. Potentiometric titration of –ArSO$_3$H and –PrSO$_3$H functionalized mesoporous silica has
been examined in methanol and methanol-water mixtures [15] and it was found that the distinct \( pK_a \) values for these catalysts in methanol coalesced when small amounts of water were added into methanol due to the inferior differentiating property of water relative to methanol. This lack of clear differentiation yielded similar activities for different acid functionalized mesoporous silica materials in cellobiose hydrolysis as the acid strength approaches the values that would be leveled in water [3]. The leveling effect occurs since the strongest cation and anion that can exist in a particular solvent are its conjugated forms and anything stronger will be leveled to their strength [31]. Therefore, it is important to determine if the leveling effect applies to the catalyst and solvent systems being characterized as this effect would eliminate differences between catalysts. Due to the above mentioned limitations of potentiometric titration, information on leveling cannot be achieved unless the conditions that hold for the ideal solution assumption, while producing reliable differentiating data, are achieved.

Systematically evaluating the titration parameters for their effect on the acidic property measurement will enable establishing appropriate characterization conditions. Average activity coefficients can be calculated by comparing measured pH values to their predicted values as a control parameter as it is not possible to determine individual activity coefficients experimentally [32]. In this work the factors affecting the acidic strength and the total acid capacity of organic acid functionalized mesoporous silica were examined to better characterize their intrinsic acidic properties thereby deconvoluting these properties from their assessment in reaction studies.

**Experimental**

For the synthesis of propyl sulfonic (-\( \text{PrSO}_3\text{H} \)), arene sulfonic (-\( \text{ArSO}_3\text{H} \)), butyl carboxylic (-\( \text{BuCOOH} \)) and ethyl phosphonic (-\( \text{EtPO}_3\text{H} \)) functionalized SBA-15 type
mesoporous silica, the functional group precursors, (3-mercaptopropyl)trimethoxysilane (MPTMS) (85%, Gelest), 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) (50% in dichloromethane, Gelest), 3-cyanopropyltriethoxysilane (CPTES) (98%, Gelest), and diethylphosphatoethyltriethoxysilane (DEPTES) (95%, Gelest) were used as purchased, respectively. The silica precursor, tetraethylorthosilicate (TEOS) (98%, Aldrich) was used without further modification in all syntheses. Control experiments were performed with Amberlyst-15-wet (Acros), propane sulfonic acid (98%, Acros) and hydrochloric acid (HCl) (16 N, Fisher), which were used as purchased.

**Synthesis of organic acid functionalized SBA-15**

The co-condensation procedure described in literature was followed for the synthesis of the SBA-15 materials with only slight modification [22, 33-35]. As a template for the silica, 4 g of Pluronic 123 (BASF Co.), a tri-block co-polymer consisting of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide), (EO)_{20}(PO)_{70}(EO)_{20}, was dissolved in 125 ml of a 1.9 M aqueous HCl solution. TEOS (8.2 ml) was introduced into the solution when the temperature reached 40 °C. After a pre-hydrolysis period of 45 min, the functional group precursor was added in a molar ratio of 0.15 relative to the TEOS. For oxidation of the thiol groups in SBA-15-PrSO_{3}H synthesis, 3 parts hydrogen peroxide (30 wt% aqueous, Fisher) with respect to TEOS was added to the mixture. The resulting mixture was stirred for 20 h and aged for 24 h under static conditions before filtration. The surfactant template was removed by total reflux in ethanol with 0.1 M HCl for 24 h. When synthesizing SBA-15-BuCOOH, the functional groups were acidified further by refluxing for 24 h in a 50 wt% aqueous H_{2}SO_{4} solution. The catalysts were recovered by filtration, washed multiple times with DI water/ethanol and oven-dried at 80°C. Lower functional group loaded samples of SBA-15-BuCOOH
and SBA-15-PrSO$_3$H were prepared by changing the precursor ratio to 7.5 and 2.5% [34]. The SBA-15-EtPO$_3$H and SBA-15-ArSO$_3$H were synthesized as reported previously [3].

**Synthesis of HMS-PrSO$_3$H**

The -PrSO$_3$H groups were also tethered on HMS-type mesoporous silica surface at two different loadings, e.g. precursor ratios of 7.5 and 15%, as described in literature [36] and denoted as HMS-PrSO$_3$H. HMS type mesoporous silica was templated using dodecylamine (98%, Acros Organics) dissolved in an ethanol-water mixture. The silica precursor, TEOS, and the functional group precursor, MPTMS, were introduced to the mixture simultaneously. The molar composition of the resulting mixture was 0.08 TEOS: 0.0275 dodecylamine: 0.89 EtOH: 2.94 H$_2$O. The molar ratio of MPTMS was 0.006 and 0.012 for the 7.5 and 15% loadings, respectively. The mixture was stirred at room temperature for 24 h, filtered and washed. The template was removed by total ethanol reflux for 24 h. The filtered and air-dried product was oxidized by hydrogen peroxide (2.04 g/g dry material) in three parts of a 1 M HCl in ethanol mixture for 24 h at 40 °C. For further acidification, the material was treated with 1 M H$_2$SO$_4$ for 4 h. The final product was recovered by filtration, washed thoroughly with water and ethanol, and oven-dried.

**Catalyst characterization**

Textural properties of the catalysts were determined from nitrogen adsorption/desorption isotherms measured at -196°C using a Micromeritics ASAP 2020 analyzer. Prior to measurement, the samples were degassed for 5 h at 100 °C. The surface area was obtained using the BET method. The pore volume and pore size distributions were calculated from the desorption branch of the isotherms according to
the BJH method as discussed in the literature [37, 38]. Incorporation of the functional
groups and removal of the surfactant were confirmed by thermogravimetric analysis in
the temperature range 50°C to 650°C with a temperature ramp of 5 °C/min under air
flow using a Perkin-Elmer TGA7. CHNS values were determined by elemental analysis
using a Perkin-Elmer Series II 2400 analyzer. For the potentiometric titrations, a
Metrohm 798 MPT Titrino automatic titrator equipped with a Metrohm combined glass
electrode (6.0233.100) was used. The electrode was calibrated with buffers of pH 4.00,
7.00 and 10.00 (Fisher) before each measurement and data were taken after the potential
signal stabilized. Each titration was performed under vigorous stirring to avoid external
mass transfer limitations. Adding a small amount of base solution initially and letting it
equilibrate for 30 min helped to reduce the noise in the titration curve. Results were
analyzed for the acidic strength and total acid capacity using the Gran Plot analysis and
the dynamic end point determination method (available through the Metrohm Tiamo
software). For the measurements above ambient temperatures, the solution vessel was
immersed in an oil bath equipped with temperature control and was attached to a total
reflux column to prevent solvent evaporation. Acidic strength and total acid capacity
values were calculated for the synthesized catalysts at varying salt concentrations (no
salt, 0.01 M, 1 M) and catalyst concentrations varying from 0.02 to 0.5 wt% at three
temperatures (25, 50, 70 °C).

Results and Discussions

Comparison of organic acid functionalized mesoporous silica with functional groups
of varying strength, as shown in Scheme 1, were incorporated onto SBA-15 and HMS
type supports via co-condensation maximum at 15% loading. Only co-condensed
materials were compared rather than grafted so as to maintain a more uniform
distribution along the channels. Previous work has shown that the functional groups tend to preferentially locate at the pore mouth when incorporated via post-synthesis grafting [39]. A maximum loading of 15 mol% of the functional groups was used in the current work as previous studies showed that high loadings of functional groups can disrupt the regular mesoporous structure [15].

![Scheme 1](image1.png)

**Scheme 1.** Functional groups incorporated onto mesoporous silica. Propyl sulfonic acid (a); arene sulfonic acid (b); ethyl phosphonic acid (c); butyl carboxylic acid (d).

The N\textsubscript{2} adsorption-desorption isotherms for the prepared materials (Figure 1) displayed Type IV isotherms, which are characteristic of mesoporous materials [39]. Moreover, H1 type hysteresis loops suggested that the functional group loadings maintained the regularity of the inorganic mesostructure. The textural properties for the synthesized materials are given in Table 1. Narrow pore size distributions were measured for all of the synthesized materials within the expected range for mesoporous materials [22, 33-35]. Median pore diameters were in the reported range as well, but varied somewhat according to the functional group. This difference was expected as one of the factors determining the pore size of the final functionalized material is the interaction of the precursors with the aqueous synthesis media during one-pot synthesis [39].
Figure 1. $\text{N}_2$ adsorption-desorption isotherms of the 15% organic acid functionalized SBA-15 materials. (○) SBA-15-PrSO$_3$H; (◇) SBA-15-EtPO$_3$H; (□) SBA-15-ArSO$_3$H; (△) SBA-15-BuCOOH.

Table 1. Textural properties of the organic acid functionalized mesoporous silica samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (%)$^a$</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>MPD (Å)</th>
<th>$V_p$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-ArSO$_3$H</td>
<td>15</td>
<td>637±13</td>
<td>60±4</td>
<td>0.61±0.12</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>744±19</td>
<td>56±3</td>
<td>0.97±0.11</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>788±20</td>
<td>59±2</td>
<td>0.86±0.08</td>
</tr>
<tr>
<td>SBA-15-EtPO$_3$H</td>
<td>15</td>
<td>625±22</td>
<td>67±3</td>
<td>0.81±0.09</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>758±18</td>
<td>54±2</td>
<td>0.90±0.07</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>744±19</td>
<td>56±3</td>
<td>0.97±0.11</td>
</tr>
<tr>
<td>SBA-15-PrSO$_3$H</td>
<td>15</td>
<td>575±12</td>
<td>77±5</td>
<td>0.83±0.05</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>613±15</td>
<td>80±2</td>
<td>0.77±0.14</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>649±24</td>
<td>81±3</td>
<td>0.82±0.05</td>
</tr>
<tr>
<td>SBA-15-BuCOOH</td>
<td>15</td>
<td>744±19</td>
<td>56±3</td>
<td>0.97±0.11</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>878±29</td>
<td>60±4</td>
<td>0.86±0.08</td>
</tr>
<tr>
<td>HMS-PrSO$_3$H</td>
<td>15</td>
<td>815±27</td>
<td>30±3</td>
<td>0.66±0.09</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>884±18</td>
<td>32±4</td>
<td>0.69±0.13</td>
</tr>
</tbody>
</table>

$^a$ Molar ratio of organic acid precursor to TEOS
The t-Plot analysis indicated the presence of micropores in the materials. Micropores in SBA-15 structures are typical and because of their small size, no functional groups are expected to reside within them [40]. In fact, the surface density plots (Figure 2), prepared according to the procedure explained by Liu and co-workers [41], suggested that the functional groups were residing on the surface of the pores thereby making them readily accessible.

**Figure 2.** Surface density of –PrSO$_3$H groups incorporated onto SBA-15 based on S content.

The functional group incorporation was further confirmed by thermogravimetric analysis, as shown in Figure 3. The first peak for each sample was associated with the desorption of physisorbed water. In previous studies, a peak around 220 °C has been observed and attributed to the presence of residual surfactant. Modification of the reflux media by adding a small amount of HCl facilitated surfactant removal and, therefore, the peak associated with the decomposition of the residual surfactant mostly disappeared as seen in Figure 3. Elemental analysis characterization indicated that even with the modified reflux method some of the carbonaceous material was retained in the samples. Therefore, C mol% was not used as an indicator of the number of incorporated functional groups. S mol% was used for SBA-15-PrSO$_3$H and SBA-15-ArSO$_3$H and the
measured sulfur contents obtained by elemental analysis were in good agreement with the molar ratios of the precursor used in the synthesis of the materials, demonstrating high incorporation yield of the functional groups. The presence of the peak at 450°C and the absence of 350°C peak proves complete oxidation of thiol groups for the -PrSO₃H functionalized materials [33]. The decomposition of the –ArSO₃H groups, which was observed at 540°C, was also consistent with the reported values [22].

**Figure 3.** Thermogravimetric analysis of the 15% functionalized mesoporous silica materials. (○) SBA-15-PrSO₃H; (◊) SBA-15-EtPO₃H; (□) SBA-15-ArSO₃H; (△) SBA-15-BuCOOH.

The acidic strength and total acid capacities of the synthesized materials were calculated using the Gran Plot and dynamic equivalence point methods. In the buffer region of the titration curve, the acid dissociation constant Kₐ is represented in the slope of the Gran Plot [42],

\[ G(v) = v \times 10^{-pH} = -K_a \times v + (K_a \times V_e) \]  

*(Equation 1)*

where \( v \) is the volume of the base added and \( V_e \) is the endpoint.

Alternatively, in the acidic region of the titration curve the Henderson-Hasselbalch equation can be used to determine the pKₐ [42],

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]  

*(Equation 2)*
where the dissociated base concentration [A\textsuperscript{-}] to the undissociated acid concentration [HA] ratio can be estimated from the ratio of base added volume/end point volume. However, the Henderson-Hasselbalch approach involves a single-point determination and has been shown to hold for a narrow region only, while the Gran Plots represent the trend from multiple data points [29]. Although Gran Plots are considered accurate for the determination of acidity constants, curve-fitting techniques are considered to be more accurate for determining the total acid capacities [32]. Therefore, the dynamic equivalence point method, which determines the end point based on the first derivative of the fitted curve, was used for the determination of total acid capacities.

Mass transfer limitations must be more rigorously addressed in the titration of heterogeneous acids relative to homogeneous acids. External diffusion limitations can be overcome with rapid stirring speeds. In order to reduce internal diffusion limitations, the basic titrant must be introduced to the system slow enough to assure that equilibrium is reached prior to the subsequent titrant injection. Addition of a salt facilitates ion-exchange thereby reducing the response time of the electrode by increasing the ion concentration. For an aqueous solution of HCl (Figure 4a), only a small amount of salt (0.001 M) was required to shorten the response time for measuring the pH value, which agreed with theoretical value that was calculated from the HCl amount added by assuming that the acid is totally dissociated and represented as H\textsuperscript{+}. At higher salt concentrations the measured pH values, namely the proton activities, will no longer represent the actual proton concentration due to the deviation of activity coefficient from unity. The same phenomenon was observed for SBA-15-PrSO\textsubscript{3}H in water at similar proton concentration (Figure 4b), but higher salt concentrations were required to achieve a rapid response time for reaching the equilibrated pH value. Even at the higher salt concentration, the response time was not as rapid as with the HCl solution. The
longer response time and higher salt concentration requirement with SBA-15-PrSO_3H were due to mass transfer.

![Figure 4](image)

**Figure 4.** Effect of salt on response time and pH for aqueous solutions of hydrochloric acid (a), and SBA-15-PrSO_3H (b). (□) DI-water; (△) 0.001 M NaCl\_aq; (◇) 0.005 M NaCl\_aq; (×) 0.01 M NaCl\_aq; (★) 0.1 M NaCl\_aq; (○) 1 M NaCl\_aq.

Extension of this study to the other organic acid functionalized SBA-15 materials resulted in similar trends. The response time of the electrode decreased with increasing salt concentration and then remained constant at higher salt concentrations, while the final pH value started to decrease. The final pH values, the shortest response time for reaching that value, and the lowest salt concentration required for that response time are given in Table 2 for aqueous solutions of the organic acid functionalized SBA-15 materials. From these data, it can be seen that the required minimum salt concentration and/or the response time is not solely a function of the acidic strength or the concentration of the catalyst, but it is determined by the final pH value of the solution, which is a combination of both factors.
Table 2. Effect of salt on response time and pH for aqueous solutions of organic acid functionalized SBA-15 materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (%)</th>
<th>Cat. conc. (mg/ml)</th>
<th>NaCl conc. (mM)</th>
<th>Response time (s)</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-PrSO₃H</td>
<td>15</td>
<td>0.20</td>
<td>10</td>
<td>64±2</td>
<td>3.34±0.02</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>5</td>
<td>62±3</td>
<td>3.49±0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>5</td>
<td>40±2</td>
<td>3.69±0.02</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.20</td>
<td>5</td>
<td>58±1</td>
<td>3.51±0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>5</td>
<td>52±2</td>
<td>3.65±0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>1</td>
<td>60±3</td>
<td>3.75±0.01</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.20</td>
<td>1</td>
<td>48±1</td>
<td>3.78±0.02</td>
<td></td>
</tr>
<tr>
<td>SBA-15-BuCOOH</td>
<td>15</td>
<td>1.00</td>
<td>5</td>
<td>60±1</td>
<td>3.99±0.01</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>1</td>
<td>42±2</td>
<td>4.34±0.01</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>2.00</td>
<td>1</td>
<td>56±3</td>
<td>4.01±0.02</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.00</td>
<td>1</td>
<td>44±4</td>
<td>4.25±0.03</td>
<td></td>
</tr>
<tr>
<td>SBA-15-ArSO₃H</td>
<td>15</td>
<td>0.20</td>
<td>10</td>
<td>68±2</td>
<td>3.22±0.01</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>10</td>
<td>62±1</td>
<td>3.35±0.01</td>
<td></td>
</tr>
<tr>
<td>SBA-15-EtPO₃H</td>
<td>15</td>
<td>0.20</td>
<td>5</td>
<td>46±2</td>
<td>3.74±0.02</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>10</td>
<td>54±2</td>
<td>3.41±0.03</td>
<td></td>
</tr>
</tbody>
</table>

A similar effect of salt introduction on response times was also observed in the buffer region of the titration curves. As shown in Figure 5a, titration curves for SBA-15-PrSO₃H with 0.005 M NaOH, introduced at three different rates, e.g. 0.01, 0.02, 0.05 ml/min, did not show any difference from each other when 0.01 M NaCl had been added, which was confirmed with the other functionalized materials as well. In the absence of salt in the titration media, the speed at which the basic solution was introduced changed the slope of the curve in the buffer region as well as the pH values in the basic regime (Figure 5b). This result suggested that the presence of salt not only facilitated the proton loss by the acid, but also the proton gain by the base.
Figure 5. Titration curves for SBA-15-PrSO₃H at different titration speeds in DI-water (a) and in 0.01M NaCl (b). (□) 0.05 ml/min; (△) 0.02 ml/min; (○) 0.01 ml/min.

Comparing the total acid capacities calculated from titration data in the presence and absence of the salt further demonstrated the role of the salt in proton uptake by the base. Greater consistency between the total measured acid capacities and the sulfur contents for the sulfonic acid functionalized materials were achieved in the presence of salt than those determined in the absence of the salt (Table 3). Even the use of slow titration rates was not sufficient to establish the equilibrium between the proton loss of the acid and the proton gain of the base without the salt. Even when the titrations were performed with a less concentrated base solution, e.g. with 0.001 M NaOH and low addition rate of 0.01 ml/min, in order to achieve more rapid equilibrium, the total acid capacity values of 0.18, 0.55, and 1.11 meq/g for the 2.5, 7.5 and 15 % SBA-15-PrSO₃H, respectively, were still lower than the measured S content. Thus, salts were needed to establish the equilibrium for proton release and uptake even at very slow rates of titrant introduction.
Table 3. Total acid capacities and sulfur molar ratios for SBA-15-PrSO$_3$H and SBA-15-ArSO$_3$H.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading$^a$ (%)</th>
<th>S content$^b$(mmol/g)</th>
<th>Total acid capacity (meq/g)</th>
<th>Titration rate (ml/min)</th>
<th>NaCl conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>SBA-15-PrSO$_3$H</td>
<td>15</td>
<td>1.20</td>
<td>1.08±0.02</td>
<td>1.01±0.03</td>
<td>0.95±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.15±0.03</td>
<td>1.18±0.04</td>
<td>1.16±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.58±0.05</td>
<td>1.32±0.03</td>
<td>1.12±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.11±0.02$^c$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>0.65</td>
<td>0.55±0.03$^c$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>0.68±0.04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.24</td>
<td>0.18±0.02$^c$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SBA-15-ArSO$_3$H</td>
<td>15</td>
<td>1.18</td>
<td>1.63±0.02</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Organic acid precursor/ TEOS ratio; $^b$determined by elemental analysis; $^c$titrated with 0.001 M NaOH$_{(aq)}$; other measurements were performed with 0.005 M NaOH$_{(aq)}$.

In contrast, excessive salt addition would be anticipated to change the activity coefficients significantly, so that the measured values no longer correspond to the proton concentration. Titrations of SBA-15-PrSO$_3$H and SBA-15-ArSO$_3$H in 0.1 M NaCl resulted in total acid capacities higher than the values estimated from sulfur content. Also, the apparent pK$_a$ value decreased with increasing salt concentration (Figure 6). Similar to the trend observed with the pH values from increasing salt concentrations as shown in Figure 4, the decrease in the apparent pK$_a$ and the increase in the acid capacity would also be explained by change in the activity coefficient. As also shown in Figure 6 for SBA-15-EtPO$_3$H, the proton activity was influenced by the amount of the catalyst present in titration media. In fact, increasing amount of catalyst in the media was found to increase the apparent acidic strength for all the different functionalized materials.
Figure 6. Effect of SBA-15-EtPO$_3$H and salt concentration on acidic strength. (□) DI-water; (×) 0.01 M NaCl$_{(aq)}$; (○) 1M NaCl$_{(aq)}$.

Figure 7 shows the proton concentrations calculated from the measured pH values assuming that the activity coefficient is equal to unity. Included are values for varying levels of added SBA-15-PrSO$_3$H (15%) and increasing salt concentrations. As can be seen from the figure, the relationship that exists between the catalyst concentration and proton concentration began to deviate from linearity as the salt concentration increased.

The average activity coefficients were estimated by taking a ratio of the measured pH values to the estimated values calculated according to the following equation [42]:

\[
(10^{\text{pH}})^2 + K_a \times (10^{\text{pH}}) = K_a \times [\text{HA}]_0
\]

(Equation 3)

To predict the pH value of a particular solution with an organic acid functionalized material the acid capacity and p$K_a$ value needs to be known. However, these values are dependent on the titration calculations, so a backward feedback process was used that required determination of acidic properties under selected conditions, estimating pH based on those properties, and comparison to its measured value through calculation of the activity coefficient. The conditions that were found for predicting pH values closest
to the measured values were 0.01 M NaCl, with 0.005 M NaOH introduced at a rate of 0.02 ml/min. These were taken as the default values for the further titrations.

Figure 7. Effect of salt on the corresponding proton activities with increasing concentration of SBA-15-PrSO₃H in (◆) DI-water; (■) 0.001M NaClₐq; (▲) 0.01M NaClₐq; (×) 0.1M NaClₐq; (★) 0.5M NaClₐq.

In Figure 8 the effect of the catalyst and salt concentrations on the activity coefficients are shown for SBA-15-PrSO₃H. These were calculated based on the acidic properties determined under the default titration conditions. Extension of the work to the other functional groups revealed that the activity coefficient was not solely dependent on the catalyst concentration, the acidic strength, or the loading density of the functional group, but it was related to the pH value of the solution, which was a combined effect of the catalyst concentration and the acidic strength and loading of the functional group. Regardless of the choice of the functional group, the activity coefficients were close to unity for catalyst concentrations the corresponded to pH values of about 3.5-4, but deviated from unity for lower values, especially when the salt concentration was more than 0.01 M. Also shown in Figure 8 are the predicted activity coefficients calculated from the Debye-Huckel equation or the extended Debye-Huckel equation (for the 0.1 M NaCl case).
Figure 8. Activity coefficients for 15 % SBA-15-PrSo3H in (■) no salt; (□) 0.01M NaCl; (■) 0.1M NaCl. (*The bars indicate the predicted values using Debye-Huckel equation.)

The Debye-Huckel limiting law equation is considered to be correct up to ionic strengths of 0.01 M, but for higher concentrations a slightly modified version is needed [43]. In both equations, the salt concentration is the major factor in the activity coefficient value, whereas the dissociated acid concentration has only a minor effect. In the case of mesoporous silica samples the acid concentration also affects the activity coefficient, which the Debye-Huckel equations were not able to predict. When determining the acidic properties, it is crucial to select the conditions that will ensure equilibrium for proton transfer and while still allowing the ideal solution assumption to be invoked. To maintain this fine balance, the above mentioned default conditions were used to titrate catalyst solutions at concentrations leading to starting pH values of 3.5.

The acidic strength and total acid capacity for the organic acid functionalized mesoporous silicas and several reference materials are shown in Table 4. As would be expected, the primary factor leading to different pKₐ values was the choice of the
incorporated acid functional group with increasing strength order having the order, –BuCOOH < -EtPO3H < -PrSO3H < -ArSO3H. When unfunctionalized SBA-15 was titrated under the same conditions used for Table 4, a definitive titration curve could not be observed due to the weak acidity of these groups and as such the technique is not appropriate for determining silanol acidity values. While the silanols do not interact directly with the base titrant, it is possible that the silanols may be having an indirect effect through interaction with the functional groups.

**Table 4.** Acidic strengths and total acid capacities of the organic acid functionalized mesoporous silica samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading(^a), %</th>
<th>pK(_a)</th>
<th>Total acid capacity meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-ArSO3H</td>
<td>15</td>
<td>2.62±0.03</td>
<td>1.20±0.06</td>
</tr>
<tr>
<td>SBA-15-ArSO3H(^b)</td>
<td>15</td>
<td>2.49±0.04</td>
<td>1.82±0.08</td>
</tr>
<tr>
<td>SBA-15-EtPO3H</td>
<td>15</td>
<td>3.56±0.02</td>
<td>0.75±0.04</td>
</tr>
<tr>
<td>SBA-15-PrSO3H</td>
<td>15</td>
<td>2.78±0.03</td>
<td>1.13±0.05</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>2.88±0.03</td>
<td>0.62±0.07</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3.06±0.02</td>
<td>0.25±0.03</td>
</tr>
<tr>
<td>SBA-15-BuCOOH</td>
<td>15</td>
<td>4.78±0.03</td>
<td>0.70±0.02</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.97±0.02</td>
<td>0.54±0.03</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>5.45±0.03</td>
<td>0.33±0.02</td>
</tr>
<tr>
<td>HMS-PrSO3H</td>
<td>15</td>
<td>2.82±0.02</td>
<td>1.05±0.08</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>2.86±0.04</td>
<td>0.55±0.03</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>N/A</td>
<td>1.78±0.05</td>
<td>2.18±0.06</td>
</tr>
<tr>
<td>Amberlyst-15(^b)</td>
<td>N/A</td>
<td>1.31±0.05</td>
<td>2.35±0.04</td>
</tr>
<tr>
<td>Propane sulfonic acid</td>
<td>N/A</td>
<td>1.57±0.06</td>
<td>N/A</td>
</tr>
<tr>
<td>HCl</td>
<td>N/A</td>
<td>~ 0.1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\) organic acid precursor/TEOS, \(^b\) measured with 1 wt% catalyst concentration in the absence of NaCl.
To examine the effect of the functional group interaction with the silanol groups on the overall acidity, the acid strengths of -Pr\(\text{SO}_3\)\(\text{H}\) groups tethered onto HMS and SBA-15 type mesoporous silicas at two different loading densities were compared. HMS-type mesoporous silica supports have smaller pore volumes with thinner walls, are less ordered, have smaller pores, and do not contain micropores as found with SBA-15 silicas \cite{1, 2, 39}. For all of the functionalized materials, the \(pK_a\) values for both silica supports were found to be similar to each other and the total acid capacities were close to the sulfur content as determined by elemental analysis. Therefore, interaction of the surface silanols with the acidic groups did not appear to play a significant role in the overall acidity properties.

In contrast, the acidic strength for -Pr\(\text{SO}_3\)\(\text{H}\) group changed when the support was changed from silica to resin. The strength of the sulfonic acid groups on Amberlyst-15, which has a polymeric backbone, was higher than that for SBA-15-Pr\(\text{SO}_3\)\(\text{H}\) \cite{17}. Given that the functional group is the same, the increased acid strength for the resin material would seem to be due to a difference in the interaction of the functional group with the support, the interaction of the support with the media, and/or the cooperative effect between the acidic groups due to higher loadings on the resin \cite{16}. In the current work, the total acid capacity for Amberlyst-15 (wet) was found to be 2.18 meq/g by titration under the default conditions. In the literature, the ion exchange capacity of this resin was reported as ca. 1.7 meq/l in the wet form \cite{21} and the density of the resin in the wet form is 770 g/l corresponding to 2.21 meq/g, which agrees well with our value. On the other hand, the \(pK_a\) value found in the current study was higher than the values reported by Koujout et al.\cite{16, 17, 28}. In those studies the neutralization enthalpies were measured using 10 wt% resin in water and they found that the sulfonic groups were acting as strong acids. The strong acidity was attributed to the presence of network
interactions between the functional groups, which occur at low levels of hydration. At higher water content levels, water molecules would be expected to interrupt these interactions leading to a decrease in acidic strength. It was not possible to perform titrations for 10 wt% of catalyst solutions in our experimental set-up, because at 10 wt% catalyst concentration a slurry mixture was formed rather than a solution not allowing for accurate electrode response. However, titration of 1 wt% resin solutions was found to yield higher pK\textsubscript{a} values. Compared to those reported by Koujout et al. [16,17,28], the lower acidic strength values obtained in dilute solutions in the current work might be due to a breakdown of the water network interactions.

The increasing acidic strength for a particular functional group with increasing functional group density loading still indicated a cooperative effect between the functional groups. The cooperative effect between -ArSO\textsubscript{3}H groups incorporated onto a polymeric backbone was reported previously and was attributed to the presence of disulfonated phenyl groups, interactions between the neighboring sulfonic acid groups, and sulfone bridges between neighboring phenyl groups at low levels of hydration [28]. Even at higher water levels, interactions among the –PrSO\textsubscript{3}H groups were reported to enhance the overall acid strength [15]. As shown in Table 4, the pK\textsubscript{a} values decreased somewhat for increasing loadings of –PrSO\textsubscript{3}H groups onto the SBA-15 structure. Extension of the study to the – BuCOOH group indicated the existence of similar interactions even for the weakest functional group.

The 15% loaded SBA-15-PrSO\textsubscript{3}H displayed lower acidic strength than its homogeneous analog, propane sulfonic acid. It was shown that tethering functional groups onto a surface led to acid strength reduction due to their limited mobility [44]. The cooperative effect seen with tethered groups was proposed to arise through the formation of ‘acid pools’ with increasing functional group loading or controlled spacing
of the groups. The acidic strength of propane sulfonic acid was found to be more similar to that of hydrochloric acid giving a strong acid that dissociates completely in water. Water is not a good differentiating solvent for strong acids since any acid stronger than the hydronium ion will be leveled to the strength of the hydronium ion, indicated by a measured pK\textsubscript{a} value equal to zero. The positive pK\textsubscript{a} values for the prepared functionalized catalysts meant that there was no water leveling effect as a portion of the acid groups remains undissociated. Therefore, different strengths in water could be measured.

While the positive pK\textsubscript{a} values for the organic acid functionalized materials in an aqueous solution indicates that there is no leveling effect taking place at room temperature, it could be possible that these catalysts would be leveled at elevated temperatures. The temperature dependency of acidic strength is expressed by [43],

\[ K_a = \exp \left( \frac{-\Delta G^0}{RT} \right) \]  \hspace{1cm} (Equation 4)

Assuming that the free energy remains constant, the natural logarithm of K\textsubscript{a} must be proportional to 1/T. The pK\textsubscript{a} values were measured at 25, 50, and 70 °C for 15 % SBA-15 catalysts to predict the acidic strength at more elevated temperatures. Extrapolated values for the acidic strength at 125 °C for the functionalized materials catalysts did not in fact indicate any leveling effect (Figure 9).
Figure 9. Extrapolation of measured $pK_a$ values to elevated temperatures for 15 % (☉) SBA-15-PrSO$_3$H; (◇) SBA-15-EtPO$_3$H; (□) SBA-15-ArSO$_3$H; (△) SBA-15-BuCOOH.

In some studies, the $pK_a$-temperature relationship was stated to be unpredictable due to the changes in the solvent auto dissociation constant with increasing temperature [45, 46]. A linear relationship was observed for the 25-70 °C results as shown in Figure 9. However, it is possible that the linearity would not be maintained up 125 °C. However, these temperatures could not be accessed with the current experimental apparatus.

**Conclusions**

Potentiometric titration with a standard base was found to provide insight into the acidic properties of organic acid functionalized mesoporous silica in an aqueous solvent. It was sown that the conditions under which the titrations are performed have to be chosen carefully as they can have a significant effect on the measured values. Unlike homogeneous acid titrations, heterogeneous acid titrations involve mass transfer limitations, which can be partially overcome by using salt ion-exchange as the salt can facilitate the proton loss of the acid and the proton uptake of the base. While salts aid in improving the titration, their extensive addition leads to activities that deviate
significantly from the actual proton concentrations. The activity coefficient was also found to deviate from unity for very acidic starting pH values, which can result from a combination of bulk catalyst concentration, functional group loading density and the acidic strength of the functional group. According to the titration data, which was obtained under the conditions meeting the above-mentioned criteria, network interactions can exist between the conjugated anions enhancing the acidic strength, while the interactions with the surface silanols did not have a significant impact on the acidic strength. When used with the proper conditions, potentiometric titration can be useful tool for characterizing the acidic properties of solid materials containing tethered acidic groups.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Award No. EEC-0813570.

References

CHAPTER 3. QUANTUM CHEMICAL MODELING OF SOLVATION OF ORGANIC ACID FUNCTIONAL GROUPS IN MESOPOROUS SILICA

A paper to be submitted to Applied Catalysis A: General

Basak Cinlar¹, Mark S. Gordon² and Brent H. Shanks¹

¹Department of Chemical and Biological Engineering, Iowa State University
²Ames Laboratory, Iowa State University

Authorship roles:
Cinlar: Primary author.
Gordon: Provided advice in computational methods.
Shanks: Principal investigator.

Abstract

Due to their high surface area, tunable pore size and uniform support structure, organic acid functionalized mesoporous silica has been extensively employed as catalysts in liquid-phase systems, but only little information is available about their solvent interactions and their acidic strengths. Investigating these properties in aqueous media is of special importance, because of the extraordinary high dielectric constant of water due to its proton mobility. Propyl sulfonic-, butyl carboxylic-, ethyl phosphonic- and arene sulfonic- functional groups attached on silica bases with and without surface silanol groups were optimized for their interaction with water using DFT with B3LYP. When the functional groups were interacting with a single water molecule only, the acidic strength for the functional groups followed the order; -PrSO₃H > -ArSO₃H > -EtPO₃H > -BuCOOH, based on the % elongation of the O-H bond. Intrinsic Reaction
Coordinates (IRC) run of hydronium ion with the conjugate base of the acids resulted in the same structure as the optimized one. When EFP/DFT (B3LYP) modeled water molecules were sequentially added to the system, after addition of the fourth water molecule the trend of the acid strength changed to - ArSO$_3$H > - PrSO$_3$H > - EtPO$_3$H > - BuCOOH. However complete solvation of the acidic proton was not attained for any of the functional groups. In order to predict $pK_a$ values, their interaction with adsorbed collidine, e.g. O-H and N-H bond distances, were calculated using MP2 with the 6-311G (ddd) basis set. The $pK_a$ values were in the range of 3.74 to 4.94 respectively; propyl sulfonic group being the strongest and butyl carboxylic group the weakest acid.

**Introduction**

Specific design of silica supported catalysts with organic functional groups for the condensed phase reaction systems is contingent upon determination of their acidic strength and their interaction with the solvent. Acidic strength of the incorporated functional groups has been determined via different experimental techniques; such as potentiometric titration [1], and spectroscopic [2-4] and calorimetric studies with probe molecules [5-7]. However, the trend of their relative strengths varies according to the method used and these techniques do not provide insight about the relationship of the acidic strength and the solute-solvent interactions. Quantum chemical calculations offer the opportunity to examine the interactions of these groups with both solvent and probe molecules in detail. Such information is of importance to optimize catalytic performance of the acidic functionalized mesoporous silica materials, especially for liquid-phase reaction systems.

Acidic strength of the incorporated functional group onto a surface is determined by the nature and the concentration of the tethered group, the nature of the backbone and
the solvent [6-10]. Techniques involving probe molecules such as temperature programmed desorption (TPD) studies, in situ FTIR and 2D solid-state NMR avoid any solvent effects [11], but the choice of probe molecule affects the relative trends among different functional groups. Carbon monoxide (CO) [12], ammonia (NH$_3$) [11, 12], triethylphosphine oxide (TEPO) [12] and pyridine [2, 3, 13] are among the probe molecules that are used to characterize propyl sulfonic (-PrSO$_3$H), ethyl phosphonic (-EtPO$_3$H), butyl carboxylic (-BuCOOH) and arene sulfonic (-ArSO$_3$H) functional groups tethered on silica surface (shown in Figure 1). According to the TPD studies with pyridine [2, 3, 13], the acidic strengths of -PrSO$_3$H and -ArSO$_3$H are close to each other, in fact -PrSO$_3$H being slightly more acidic, whereas $^{31}$P- MAS NMR studies with TEPO as probe molecules revealed that the strongest acidic group was -ArSO$_3$H. Furthermore, the order of increasing acidic strength was -ArSO$_3$H > -PrSO$_3$H > -EtPO$_3$H > -BuCOOH. This agrees with previous results obtained by potentiometric titration in aqueous media.

![Figure 1: Organic-acid functionalized groups on mesoporous silica structures](image)

Although 2D solid state NMR is a powerful technique to measure the acidic strengths, it does not account for the solute-solvent interactions. These interactions not only affect the strength of the catalytic site, but they also change its nature by changing the solvent retention capacity around it [14]. -ArSO$_3$H groups are expected to be more acidic due to the presence of more electronegative phenyl group attached to sulfonic acid [15, 16].
However, -PrSO$_3$H functionalized mesoporous silica showed better activity for the etherification of benzyl alcohols [16]. The higher catalytic activity was attributed to increased hydrophobicity of sulfonic acid moieties and enhanced diffusion of reactants and products by lowering the water retention capacity around the catalytic sites.

Due to the extraordinary properties of hydrated protons [17-19], the charge stabilization capacity of water is higher than most solvents, causing the cation to be shielded. When the acid is ionized it produces a hydrated proton that has the ability to be an active site in the solution phase away from the catalyst surface [18, 20, 21]. Thus locating the protons when they are fully solvated in water is necessary to determine anion-cation interactions taking place on the catalytic surface.

Quantum chemical calculations enable studies of one-to-one interaction of the functional group with either the probe molecule or solvent molecule. Recently, Yeragi [22] used Restricted Hartree-Fock (RHF) and Moller-Plesset second order perturbation (MP2) techniques to simulate the sorption of pyridine and collidine on acidic functional groups in mesoporous silica. The adsorption energy of pyridine, the dissociation of the O-H bond, and the O-H bond deformation upon collidine adsorption were the parameters used to characterize the acid strengths of functionalized mesoporous silicas. The results confirmed the results with TPD studies using pyridine as probe molecule, yet were unable to predict the trend of acidic strengths in water.

In this work, the interaction of propyl sulfonic (-PrSO$_3$H), ethyl phosphonic (-EtPO$_3$H), butyl carboxylic (-BuCOOH) and arene sulfonic (-ArSO$_3$H) functional groups with water are studied using Effective Fragment Potential method with density functional theory (DFT). Effective Fragment Potential method accounts for both the interactions between the solvent molecules as a continuum and the interactions between
the solute and solvent molecules as individual interactions. The simulations were performed on two different models, in which the functional groups were tethered on a silica surface capped with and without surface silanols in order to determine the cooperative effect of silanols with the functional groups. Thereby it is aimed to clarify the ongoing trend for acidic strength among the functional groups, to explain their interaction with water and to explore the extent of solvation.

**Computational Methods**

The four functional groups, (-PrSO$_3$H, -BuCOOH, -ArSO$_3$H, -EtPO$_3$H) attached to silica base were constructed using MacMolPlot[23]. For all functional groups the silica base was modeled in two different ways; by hydrogen-capping all the oxygen atoms surrounding the central silicon to which functional groups is attached and by hydrogen-capping all the silicons adjacent to oxygen atoms that are attached to the central silicon. These structures and their corresponding conjugate bases were optimized with the Restricted Hartree Fock (RHF) method using the 6-311G basis set with 3 d-polarization functions in GAMESS [24]. Also, water and hydronium ion structures were optimized with the RHF method using the same basis set. Initially, simulations were run with hydronium ion and the conjugate base structures of the functional groups to optimize the location of the proton.

The RHF modeled structures with surface silanols are further refined with second order Moller-Plesset perturbation with the same basis set and their interaction with pyridine is examined to study the effect of the silanols in one-to-one interaction. The O-H and N-H bond elongations are used to predict the $pK_a$ values as described in literature [22].
In order to model the solute-solvent interactions, the structures were optimized in the presence of one water molecule using Density Functional Theory (DFT) with Becke’s 3 parameter functional (B3LYP). The RHF optimized structures were used as an initial model for these calculations. The relative acidic strengths were expressed by the elongation % of the O-H bond, which was calculated from the O-H bond lengths in the absence and presence of water.

To the DFT-optimized structures containing surface silanols, EFP/DFT (B3LYP) modeled water molecules were added one by one; up to a total of 4 EFP waters and the systems were optimized again in order to measure the O-H bond elongation. IRC runs were also performed to ensure the minimum energy state. In order to locate the global minimum in the presence of multiple water molecules, Monte Carlo simulations were run.

**Results & Discussion**

**Modeling of silica**

The DFT-optimized structures for the organic acids attached to different silica bases are shown in Figure 2. The choice of these model structures was based on the idea of maximizing and minimizing the cooperative acidic strength with the support. Experimentally, three types of silanol groups were identified for this type of supports: isolated, geminal and hydrogen-bonded. When two hydroxyl groups are bonded to the same silicon atom, they are known as geminal silanols [25]. Hydrogen-bonded silanol groups, which must be within 3Å of one another, are less reactive towards surface modification [25]. The surface silanol density depends on the synthesis method. Silanol groups can act as Bronsted acids, hydrogen-bond donors, or hydrogen-bond acceptors [26]. Ong et al. [26] used second harmonic generation to study the silica/water interface
and reported \( pK_a \) values of 4.5 for 19% of the silanol groups and 8.5 for 81% of them. As a result, the presence and nature of the silanol groups can alter the overall acidic strength.

![Figure 2](image)

**Figure 2.** DFT optimized acid functional group structures, (a-d) with silanol groups, (e-h) without silanol groups, from left to right: -PrSO₃H (a&e), -ArSO₃H (b&f), -EtPO₃H (c&g), -BuCOOH (d&h).

The re-optimized structures in the presence of a single water molecule are presented in Figure 3. Due to the interaction of the water molecules with the acidic proton, the bond distance of between the O and the acidic H increased. This increase is an indicator of the acidic strength: the larger the bond elongation the higher the acidic strength. Therefore by comparing the non-elongated O-H bond distance to the elongated O-H bond distance in the presence of water, % elongation values were calculated and are presented in Table 1. Unexpectedly, the strongest acid is –PrSO₃H due to its highest % bond elongation. Regardless of the silica base type, the trend of decreasing acidic
strength followed -PrSO\(_3\)H >-ArSO\(_3\)H > -EtPO\(_3\)H > -BuCOOH. Excluding the effect of solvent and examining one-to-one interaction with water molecule as a probe, the strengthening effect of the electron withdrawing phenyl group diminished. The type of silica model affects the elongation, in fact to a different extent for each functional group. The effect of the surface silanol groups is more significant for the weakest acid, – BuCOOH, and becomes less significant with the increasing strength of the functional group. However, the presence of surface silanol groups did not change the trend.

**Figure 3.** DFT optimized acid functional group structures with water, (a-d) with silanol groups, (e-h) without them, from left to right: - SO\(_3\)H (a&e), - phSO\(_3\)H (b&f), - PO\(_3\)H\(_2\) (c&g), - BuCOOH (d&h).

These results agree with the previous modeling studies simulating the collidine adsorption on these functional groups at MP2 level [22]. However, the silica base model
used in that study did not contain any silanol groups, instead all silanol groups were
capped with methyl groups. As the previous results indicated, the interactions with the
support affect the acidic strength. Therefore the collidine adsorption studies were
repeated for the functional groups without capping the silanol groups.

**Table 1.** Bond distances (B.D.) and % elongations according to RHF optimized water-
functional group systems.

<table>
<thead>
<tr>
<th>silanols uncapped</th>
<th>-PrSO$_3$H</th>
<th>-ArSO$_3$H</th>
<th>-EtPO$_3$H</th>
<th>-BuCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H B.D. (Å)</td>
<td>0.9761</td>
<td>0.9700</td>
<td>0.9689</td>
<td>0.9584</td>
</tr>
<tr>
<td>Elongated B.D. (Å)</td>
<td>1.0455</td>
<td>1.0381</td>
<td>1.0204</td>
<td>1.0027</td>
</tr>
<tr>
<td>Elongation %</td>
<td>7.11</td>
<td>7.02</td>
<td>5.32</td>
<td>4.62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>silanols capped</th>
<th>-PrSO$_3$H</th>
<th>-ArSO$_3$H</th>
<th>-EtPO$_3$H</th>
<th>-BuCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H B.D. (Å)</td>
<td>0.9706</td>
<td>0.9629</td>
<td>0.9661</td>
<td>0.957</td>
</tr>
<tr>
<td>Elongated B.D. (Å)</td>
<td>1.0384</td>
<td>1.0299</td>
<td>1.0159</td>
<td>1.0002</td>
</tr>
<tr>
<td>Elongation %</td>
<td>6.99</td>
<td>6.96</td>
<td>5.16</td>
<td>4.51</td>
</tr>
</tbody>
</table>

**Collidine sorption studies**

Since collidine is hydrogen-bonded, the extension of the O-H bond upon collidine
adsorption is also an indicator for the acidic strength [27] and in this case there are no
solvation effects involved. The MP2 optimized structures with surface silanol groups in
the presence of collidine are shown in Figure 4. The O-H bond stretching was calculated
by computing the difference between the O-H bond lengths in the absence and presence
of collidine and is tabulated in Table 2.
**Figure 4.** MP2 optimized acid functional group structures with collidine adsorbed: - PrSO$_3$H (a), - ArSO$_3$H (b), - EtPO$_3$H (c), -BuCOOH (d).

**Table 2.** O-H bond distances (B.D.) and % elongations according to MP2 optimized collidine adsorbed functional group systems.

<table>
<thead>
<tr>
<th></th>
<th>- PrSO$_3$H</th>
<th>- ArSO$_3$H</th>
<th>- EtPO$_3$H</th>
<th>- BuCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H B.D. (Å)</td>
<td>0.9761</td>
<td>0.9700</td>
<td>0.9689</td>
<td>0.9584</td>
</tr>
<tr>
<td>Elongated B.D. (Å)</td>
<td>1.0467</td>
<td>1.0383</td>
<td>1.0193</td>
<td>0.9997</td>
</tr>
<tr>
<td>Elongation %</td>
<td>7.23</td>
<td>7.04</td>
<td>5.20</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Furthermore, Lorente et al. [28] have correlated the $pK_a$ values to the O-H and N-H bond lengths, which were predicted from the $^{15}$N NMR spectroscopy by identifying the chemical shifts of collidine adsorbed on different type of carboxylic acids. The equation is,

$$pK_a = -3.5 \left( r_{O-H} - r_{N-H} \right) + 2.8$$  \hspace{1cm} (Equation 1)

Table 3 lists the calculated $pK_a$ values and compares them to the results obtained by previous simulation studies [22] and experimentally by potentiometric titration. The inclusion of the surface silanol groups in the model contributed to the overall acidity, as indicated by lower $pK_a$ values and made the $pK_a$ values closer to the experimental values in all cases, but the difference between the measured and computed values remained significant. As a result, one-to-one interaction with the probe molecules does not reflect the behavior of these catalytic sites in water, regardless of the silica base
modeling. A model that accounts for solvent-solvent interactions in continuum is necessary.

**Table 3:** Estimated $pK_a$ values

<table>
<thead>
<tr>
<th></th>
<th>-PrSO$_3$H</th>
<th>-ArSO$_3$H</th>
<th>-EtPO$_3$H</th>
<th>-BuCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H bond distance (Å)</td>
<td>0.9761</td>
<td>0.97</td>
<td>0.9689</td>
<td>0.9584</td>
</tr>
<tr>
<td>N-H bond distance (Å)</td>
<td>1.2447</td>
<td>1.3414</td>
<td>1.5318</td>
<td>1.567</td>
</tr>
<tr>
<td>$pK_a$ predicted</td>
<td>3.74</td>
<td>4.1</td>
<td>4.77</td>
<td>4.93</td>
</tr>
<tr>
<td>$pK_a$ [22]</td>
<td>3.91</td>
<td>4.31</td>
<td>4.94</td>
<td>5.2</td>
</tr>
<tr>
<td>$pK_a$ (experimental)</td>
<td>2.87</td>
<td>2.65</td>
<td>3.56</td>
<td>4.78</td>
</tr>
</tbody>
</table>

**Solvation with EFP/DFT water molecules**

The EFP/DFT modeled water molecules were added to the functional groups tethered on the silica surface with surface silanol groups one by one, and the bond elongations were measured after each addition. Up to three water molecules the trend of relative acidic strength remained the same. Upon the addition of the fourth water molecule, the % O-H bond elongation in -ArSO$_3$H exceeded the elongation in –PrSO$_3$H. The weakest group was still –BuCOOH. The optimized structures with four water molecules are shown in Figure 5 and the elongation values are tabulated in Table 4.

The higher strength of the –ArSO$_3$H is due to the interaction of water with the electron withdrawing phenyl ring as can be seen in Figure 5. In the absence of any EFP water molecules, the ring attracts the proton on the sulfonic acid group, as can be seen by comparing the O-H bond distances of optimized -PrSO$_3$H and -ArSO$_3$H structures alone. The O-H bond distance in the optimized –PrSO$_3$H structure is shorter than the distance in the optimized –ArSO$_3$H structure. By attracting the proton, the phenyl ring makes the proton less acidic for one-to-one interactions with water. In the presence
multiple EFP water molecules, the ring attracts the water molecules by itself. Once the phenyl ring interacts with the water molecules, the proton on the sulfonic acid is no longer withdrawn by the ring and thus becomes more acidic. At the same time, the ring breaks the interaction of water molecules with each other and allows a more intimate contact of the water molecule with the acidic proton.

![Figure 5. DFT optimized acid functional group structures with 4 EFP/DFT water molecules: -PrSO$_3$H (a), -ArSO$_3$H (b), -EtPO$_3$H (c), -BuCOOH (d)](image)

Whereas the hydrogen-bonded network for water is more or less distracted for the -ArSO$_3$H and -PrSO$_3$H models, the water structure as continuum is more recognizable with -EtPO$_3$H and is almost completely present in the case of -BuCOOH. In both cases, the water structures do not interact directly with the functional group by themselves, but support the first water molecule that is in contact with the functional group. The
presence of the EFP waters changes the bond elongation, but not as significantly as it changed the -ArSO\textsubscript{3}H and -PrSO\textsubscript{3}H.

**Table 4.** Bond elongations according to EFP/DFT optimized water and DFT optimized functional group systems.

<table>
<thead>
<tr>
<th></th>
<th>-PrSO\textsubscript{3}H</th>
<th>-ArSO\textsubscript{3}H</th>
<th>-EtPO\textsubscript{3}H</th>
<th>-BuCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H B.D (Å)</td>
<td>0.9761</td>
<td>0.9700</td>
<td>0.9689</td>
<td>0.9584</td>
</tr>
<tr>
<td>Elongated B.D (Å)</td>
<td>1.0555</td>
<td>1.0553</td>
<td>1.0225</td>
<td>1.0077</td>
</tr>
<tr>
<td>Elongation %</td>
<td>8.13</td>
<td>8.79</td>
<td>5.53</td>
<td>5.15</td>
</tr>
</tbody>
</table>

Although the bond elongation values increased with further addition of water molecules, a complete dissociation for the proton from the functional group was not observed. According to simulations of ionization conducted by Paddison [29], six water molecules are required to start to shield the proton (as a hydronium ion) from direct electrostatic charges with the anion. The complete shielding of the proton will occur with 22.5 water molecules and shielding of the proton allows it to move away from the anion and the hydrated proton is free to catalyze reactions in the bulk away from the support surface. Such an effect could not be observed by simulating only 4 water molecules.

Studies with higher number of water molecules enable a more realistic approach for determination of acidic strength. Furthermore, if a mathematical relationship between the % bond elongation and pK\textsubscript{a} values can be established, the effect of water molecules on the acidic strength, and thereby the stabilization capacity of water, can be outlined quantitatively. However, EFP/DFT studies were already computationally expensive regarding the number of atoms in the model groups. In order to model the fully hydrated
system, simulations with the Monte Carlo method are strongly preferred for locating the global minimum.

The Monte Carlo method involves random displacement of the water molecules followed by geometry optimization and the geometry with the lowest total energy is accepted as the global minimum. The final optimized structure depends on the initial structure and different minima are obtained with different initial geometries. Therefore multiple Monte Carlo simulations have to be performed until the same global minimum is reached.

The DFT optimized functional groups attached onto a silica base with silanol groups were inserted in a water cluster with 26 members, modeled with EFP/DFT for locating the global minimum. The geometry optimizations resulted in accumulation of most of the water molecules around the silanol groups and global optimization could not be attained due to the proton tunneling effect taking place between the water molecules and silanol groups. Different initial geometries did not resolve the problem, rather a limitation on the randomization of water molecules is required that is not possible in the classical Monte-Carlo approach.

Alternatively, a -PrSO$_3$H group attached onto silica support with capped silanol groups was modeled in a water cluster of 26 members using the Monte Carlo method and the problem regarding the proton tunneling effect was not encountered. In this case a uniformly distributed water cluster surrounding the functional group was attained as the global minimum. However, multiple Monte Carlo simulations are needed for ensuring the global minimum that will be the future aspects of this work.

Conclusions
The interaction of water and organic acid functional groups tethered on a silica base were simulated with quantum chemical techniques; DFT and EFP/DFT with B3LYP where RHF optimized structures were used as an initial model. According to the DFT-optimized structures, the proton remains on the functional group when water molecule interacts with them. According to the bond elongation percentages on the optimized structures with DFT, the acidic strength is in the order of; - PrSO$_3$H > - ArSO$_3$H > - EtPO$_3$H > -BuCOOH, regardless of the modeling of the silica base. When 4 EFP/DFT (B3LYP) optimized water molecules were introduced, the acidic strength order altered in the following way: - ArSO$_3$H > - PrSO$_3$H > - EtPO$_3$H > -BuCOOH, based on the bond elongation percentages. Complete solvation was not observed having only 4 water molecules per acid group. Collidine adsorption studies using MP2 provided a way to correlate $pK_a$ values of the acidic groups to the extension of the O-H bond upon adsorption. The $pK_a$ values followed the order - PrSO$_3$H > - ArSO$_3$H > - EtPO$_3$H > -BuCOOH regardless of the silica base model.

References

CHAPTER 4. KINETICS OF MONOSACCHARIDE CONVERSION
IN THE PRESENCE OF HOMOGENEOUS ACIDS

A paper to be submitted to Journal of Catalysis

Basak Cinlar¹, Cody Jensen², Brandon Peters³ and Brent H. Shanks¹

¹Department of Chemical and Biological Engineering, Iowa State University
²Department of Chemical and Biological Engineering, Iowa State University (formerly)
Chemical and Biological Engineering Department, University of Illinois-Urbana,
Champagne (currently)
³Department of Chemical and Biological Engineering, Iowa State University (formerly)

Authorship roles:
Cinlar: Primary author.
Jensen, and Peters: Second and third authors, provided help with the kinetic studies.
Shanks: Principal investigator.

Abstract

For the utilization of biomass in the fuel and polymer industry, a wide variety of catalysts has been studied for their activity either on the dehydration reaction in particular or on the monosaccharide degradations in general. Yet, systematic data outlining the effects of acidic features is not available and a common framework for catalytic activity comparison is missing that is inevitable for rational catalyst design. The current work aimed to provide insight about the effect of the nature of acid and initial acidity on degradation kinetics of C-5 and C-6 carbohydrates and thereby built a platform allowing activity comparison. Mineral and organic acids ranging in acidic strength, hydrochloric, sulfuric, phosphoric, maleic, and propane sulfonic acid were
tested for their activity in degradation of xylose, fructose and glucose at two different pH values; 1.5 and 3.6. In the presence of weak homogeneous acids, glucose undergoes degradation through a different mechanism at pH of 1.5 than at pH 3.6. Such a mechanism change does not occur in the presence of strong homogeneous acids. On the other hand, xylose and fructose undergo degradation via single mechanism regardless of the pH or nature of the homogeneous acid. Regardless of the acid type and strength, the activation energies were approximately 140 kJ/mol for fructose and xylose. A common framework that compiles the catalytic activities and outlines the differences related to underlying mechanism changes provides the basis required for rational heterogeneous catalyst design.

**Introduction**

Dehydration of monosaccharides to furanic compounds has regained considerable interest in the past decade either as a reaction which provides valuable products for the renewable fuel and polymer industry or as one of the degradation reactions accompanying polysaccharide hydrolysis [1]. Studies considering dehydration as a side reaction during saccharification focus on how to minimize its occurrence while the dehydration reaction studies by itself has a complete opposite focus, that is how to achieve higher yields at high conversions. In both regards, a wide variety of catalysts ranging from traditional strong mineral acids to novel ionic liquids immersed on silica supports have been examined [2, 3]. However, only few of these studies report systematic data that compared catalytic performances on a common framework and provided insight about the reaction system. Neither are the acidic features of the catalysts outlined to provide tools for the rational design of a novel catalyst. Using both mineral and organic acids of varying strength at different pH levels, the effects of
different acidic features can be investigated for the hydrothermal degradation of glucose and xylose, which are the most common products of biomass hydrolysis. Further knowledge is gained by comparing their kinetics to the well-understood fructose degradation kinetics. Thereby, not only a common framework for catalytic activity comparison is built, but also guidelines for a rational catalyst design regarding the acidic properties are provided, that constitute the focus of this study.

Saccharification, hydrolysis of polysaccharides into monosaccharides, is a common first step for the valorization of agricultural lignocellulosic waste products [4, 5]. While the cellulosic compounds lead to glucose, hydrolysis of hemicellulosic compounds also produces xylose and arabinose beside the C6 sugars, e.g. glucose, galactose and mannose. Utilization of traditional mineral acids, such as hydrochloric and sulfuric acids, causes degradation of the monosaccharides readily at the hydrolysis conditions, among which dehydration of C5 and C6 sugars into furfural and hydroxymethylfurfural takes place also. Some of the other degradation reactions occurring in conjunction with the dehydration reaction are condensation, fragmentation and polymerization reactions that result in, but are not limited to glyceraldehyde, glycolaldehyde, pyruvaldehyde, formaldehyde, levoglucosan, levulinic acid, acetic acid and formic acid [6]. Side reactions accompanying cellulose hydrolysis and glucose dehydration are summarized in Scheme 1.

Including dehydration, all monosaccharide conversion reactions are acid catalyzed and have very similar activation energies [7]. This fact further creates a problem in the monosaccharide dehydration and prevents the commercialized HMF production from glucose. Due to the shortage of petroleum supplies, HMF production from biorenewable resources has regained interest, because it is classified as one of the primary building blocks for the polymer industry along with furfural [1, 8]. Recently, several attempts
with a wide range of novel catalysts were made to achieve high yields of furanic compounds [9-11]. Also, considerable amount of past literature investigated the monosaccharide conversion, or in particular dehydration, but few links have been established in the more recent studies with heterogeneous catalysts to these studies with homogeneous acids [3, 6, 8, 12]. The difference in the reaction conditions and lack of data about the intrinsic values such as activation energies and turnover numbers account for the absence of such links. Systematic evaluation of data in that regard will provide valuable insight about the acidic features affecting the reaction yields.

Scheme 1. Reaction scheme for cellulose hydrolysis and glucose degradation reactions.

Parameters that are thought to play a role on the yield of the dehydration, and the conversion reactions in general are temperature, nature of the solvent, and the type and the concentration of the acid [4, 13-16]. The effect of different acids on dehydration has been demonstrated by Dumesic and co-workers where they tested HMF formation from
fructose in the presence of different mineral acids [16]. In experiments at pH 1.5 in DMSO-water mixture with an extracting phase, phosphoric acid showed highest selectivity at 170°C followed by hydrochloric acid. Sulfuric acid showed lowest selectivity under these conditions. Accordingly it was concluded that selectivity was affected by the choice of the acid. However, these selectivity values were reported at different conversions that lead to the question of whether the conversion or the acid itself is responsible for the variation in the selectivity.

Another study about the effect of the choice of the acid on the reaction selectivity examined organic acids, including dicarboxylic acids, and compare their activity to that of sulfuric acid [5]. While acetic acid did not show any activity for the hydrolysis, maleic acid did, which was explained by its di-acidic character enhancing activity via enzyme mimicking acid-base properties. Surprisingly, maleic acid did not show any activity on glucose degradation and hence it was claimed to be a superior catalyst with higher selectivity for cellulose hydrolysis as compared to sulfuric acid. Also butyl carboxylic acid functionalized mesoporous silica catalysts showed better selectivity as compared to other organic acid functionalized mesoporous silica, but the rates with the butyl carboxyl functionalized material were too low that no significant yield could be obtained [17]. The ability to selectively hydrolyze cellulose compounds without degradation is not claimed with other homogeneous or heterogeneous acids. In fact, in many studies [8,12,14,15] both hydrolysis and the accompanying reactions converting monosaccharides further were directly proportional to the number of available protons regardless of the type of the acid used, which is in contrast with the findings of the studies with dicarboxylic acids [5].

Moreover, studies on glucose conversion with dicarboxylic organic acids revealed that the rates were independent of the pH when organic acids were used, but in the
presence of sulfuric acid there was a direct relationship between the measured reaction rate and pH. Similarly, Bobleter and Bonn reported pH-dependent reaction regimes of glucose degradation when sulfuric acid was used, but in the presence of acetic acid such dependency could not be recognized [14]. Difference in the rates due to the choice of catalyst was reflected in the activation energies also, and the difference in the activation energies was attributed to different mechanisms, but details about the mechanism change were not mentioned [5]. The same studies on xylose resulted in two different activation energies for sulfuric acid and maleic acid also; again the reason was not clarified [18].

Different mechanisms have been proposed for the glucose degradation. According to one hypothesis, glucose dehydration occurs from the acyclic form via a 1, 2 enediol intermediate which is also the intermediate in the fructose dehydration [19]. The slower dehydration rates of glucose as compared to fructose were explained by the lower concentration of the open-chain form due to higher ring stability. Another hypothesis suggests that glucose isomerizes to fructose first via hydride shift and subsequently follows the same degradation mechanism with fructose. Donald et al. mentioned a hydrogen transfer from C2 to C1 during the conversion of aldoses to furfural derivatives which can account for 28% of the reaction proceeding via the ketose [20]. The active forms for dehydration were considered to be the furanose structure for C6 sugars and pyranose structure for the C5. The higher ratio of the xylopyranosyl form was used to explain the slower reaction of glucose compared to xylose, but it does not predict any change in the relative rates according to type of the acid. In some studies the glucose dehydration rate reported was about half the xylose dehydration rate, while in others a much slower relative rate was reported.
The discrepancy in the relative rates can be extended further. While comparable HMF yields were obtained from glucose and fructose at 175-390°C in the presence of 10^{-2} M mineral acids with or without organic extracting phase, a good yield of HMF is obtained only from fructose at 85-90°C in the presence of >0.25M strong mineral acids [3]. Under these conditions HMF yields from glucose or other aldohexoses were very small. Whether it is the high temperatures and (or) low proton concentration that caused the change in the relative rate trends remained elusive.

In this study, the effects of the nature of acid and initial acidity on degradation kinetics were outlined by studying organic and mineral acids of different strength for their activity on glucose, fructose and xylose at two different proton concentrations, pH 1.5 and 3.6. Sulfuric acid, hydrochloric acid were chosen as strong mineral acids, phosphoric acid as weak mineral acid, and maleic acid and 1-propylsulfonic acid as weak organic acids. By studying the effects of these acids under the same conditions the effect of proton concentration was deconvoluted from the effect of the acidic strength. Furthermore, calculating the activation energies for a temperature range 145-175°C, the observed activities could be related to the proposed mechanisms. Thereby, this study builds a platform for activity comparison and provides a reference point for heterogeneous acid design.

**Experimental**

Hydrochloric acid (12N, Fisher Chemicals), sulfuric acid (18N, Fisher Chemicals), o-phosphoric acid (85%, Fisher Chemicals), maleic acid (99%, Acros), and 1-propanesulfonic acid (99%, Acros) were used as purchased. The reactants, D-fructose (Fisher Chemicals), D-xylose (Acros) and α-D-glucose (99%, Acros), were also used as purchased without further purification.
For the kinetic experiments aqueous solutions of hydrochloric acid, sulfuric acid, phosphoric acid, maleic acid, and 1-propanesulfonic acid at two different pH values, 1.5 and 3.6, were prepared. The pH values of the solutions were measured by combined glass electrode (6.0233.100, Metrohm) attached to a Metrohm 798 MPT Titrino automatic titrator. Before each measurement the electrode is calibrated using three standard buffers at 4.00, 7.00 and 10.00.

Kinetic experiments were performed at 145, 160 and 175°C in a 250 ml stirred batch reactor (Parr Assoc.) equipped with a glass liner. Temperature control was maintained with a PID controller attached to heating jacket and cooling coil. The corresponding sugar amount for a final concentration of 0.11M was added to the acidic solution before charging to the reaction vessel. Time zero was taken as the time when the desired reaction temperature was reached and conversion at that time was taken to be zero. The reactor was pressurized with 300 psig nitrogen pressure to ensure condensed phase. Besides, stirring speed was adjusted to overcome external mass transfer limitations as initial screening. Samples that were collected during the kinetic runs were filtered through 0.2µm nylon filter (Cobert Assoc.) and the pH back-adjusted to 6-7 by addition of 4.0 M NaOH prior to HPLC analysis.

The samples were analyzed with a Hi-Plex H⁺ column (Polymer Lab.) at 65°C with a Waters HPLC system equipped with Waters 2414 Refractive Index detector (RID) and Waters 996 Photoiodide Array Detector (PAD). The mobile phase was 10mM sulfuric acid solution flowing at 0.6 ml/min. While the RID peak areas and intensities were used to estimate the sugar concentration to avoid peak convolutions in the presence of weak acids, dehydration product concentrations were determined using both PAD peak areas at 280 nm (conc. <0.2wt%) and RID peak areas (conc. >0.2wt%) to maintain linear
relationship of the peak area or intensity with the concentration. The glucose concentrations in the samples were confirmed with the Bio-Rad Glucose Analyzer also.

**Results and Discussion**

Reactions involving conversion of monosaccharides are all acid-catalyzed; in fact the reaction rates are proportional to the number of available protons. Previously, the activity of maleic acid was compared to the activity of sulfuric acid for cellobiose hydrolysis and glucose degradation in the presence of equal amounts of acid instead of equal number of protons [5]. Being a weak acid with a dissociation constant of 1.97 at room temperature, the same amount of maleic acid lead to higher pH values compared to sulfuric acid. In that regard, the lower activity in the presence of maleic acid was expected, and does not necessarily indicate that maleic acid is a less powerful proton source for the degradation reaction. A better comparison can be achieved by measuring their catalytic activities at equal number of protons. Therefore this study compared the acid activities at the same pH values rather than at the same molar acid amounts.

The acids used in this study were hydrochloric, sulfuric, phosphoric, maleic and 1-propanesulfuric acid. Due to complete dissociation of hydrochloric acid and sulfuric acid as strong acids, the pH value for these solutions at the reaction temperature is not expected to differ as much as the value for weak acids when compared to their room temperature pH value. For strong acids, the only reason for the decrease in the pH value upon heating will be the change in the activity coefficient. However, the pH at the reaction temperature is expected to be lower than the ambient pH in the presence of weak acids, considering the effect of temperature on $pK_a$. The $pK_a$ values of the acids used in this study are shown in the Table 1 at room and elevated temperatures.
Table 1. Reported and estimated first acid dissociation constants and pH values at 175°C of the acids used in this study. (a) Numbers in parentheses are the temperatures (°C) for the reported values [29]. (b) Estimated values, (c) Not a reported value, experimentally measured

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a,1$ (a)</th>
<th>$pK_a$ at 175°C (b)</th>
<th>pH at RT</th>
<th>pH at 175°C (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>-4.0 (25)</td>
<td>N/A</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.60</td>
<td>3.60</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>-3.0 (25)</td>
<td>N/A</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>2.12 (25)</td>
<td>2.05</td>
<td>1.50</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>2.09 (75)</td>
<td></td>
<td>3.60</td>
<td>3.57</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>1.94 (25)</td>
<td>1.78</td>
<td>1.50</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>1.89 (75)</td>
<td></td>
<td>3.60</td>
<td>3.55</td>
</tr>
<tr>
<td>1-Propanesulfonic acid</td>
<td>1.57 (25)</td>
<td>1.41</td>
<td>1.50</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>1.52 (50)</td>
<td></td>
<td>3.60</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Assuming a linear relationship between the ln $K_a$ value and the reciprocal temperature according to the Henry’s Law, the $pK_a$ values were extrapolated to 175°C, which is the highest temperature used in this study, and the corresponding pH values were calculated. The change in the pH values upon heating and its potential effect on the rates were determined to be within the experimental error margin. Therefore the change in the pH of the solution due to increase of $pK_a$ or activity coefficient is neglected and results were interpreted as if the final proton concentrations in the experimental runs at different temperatures were equal.

The two different proton concentrations, pH 1.5 and 3.6, were chosen to cover most of the pH range used in the literature. Commonly, kinetic and mechanistic studies regarding the monosaccharide degradation or dehydration were conducted in the presence of strong mineral acids, lowest being 50mM. 50mM sulfuric acid corresponds to a pH value of 1.5 approximately. On the other hand, the more recent studies with the
heterogeneous catalysts were performed at much higher pH values. The exact proton concentrations in the presence of heterogeneous catalysts such as ion-exchangers and zeolites were not reported. However, the pH values were reported for organic acid functionalized mesoporous silica when used for cellobiose hydrolysis and range from pH 3.0 to 4.5 approximately. Studying the proton activity at pH 1.5 and 3.6 captured a big portion of the literature and enabled to bridge between the results with homogeneous acids and heterogeneous acids. Lower pH values than 1.5 were not preferred due to the difficulty of achieving them with the weak acids.

A similar approach was followed for the choice of temperature range. Although some mechanistic studies were carried out at much higher temperatures such as 390°C [21], the heterogeneous catalysts are mostly not hydrothermally stable at such high temperatures. Indeed, investigation of the kinetic at lower temperatures, which can be used in heterogeneously catalyzed studies as well, provides more useful data. However, reaction rates at 145°C are rather difficult to determine. The size of the error bars can shade the change in the rates if not carefully analyzed. Besides, at such lower rates of reaction, the kinetics can be easily changed by the formation of acids during the reaction. These acids self-catalyze the reaction and cause unexpectedly higher rates. At higher temperatures, and hence higher decomposition rates, the formation of these acids is insignificant [12]. Overall, comparing the activation energies is a more reliable way for understanding the effect of acidity rather than comparing the relative rates at a single temperature.

In Figures 1 and 2 showing the decomposition of monosaccharides at different temperatures, the conversions were readjusted to zero at the time zero which was taken as the time at which the desired reaction temperature was reached. Such an adjustment allowed easier comparison of the relative trends among the different monosaccharides.
In reality, the reactants were charged to the reactor initially and some conversion occurred during the heat-up period. The initial loss was determined to be less than 10% and was insignificant compared to the total conversion during the time of actual reaction run.

**Figure 1.** Sugar (glucose (a), xylose (b), fructose (c)) conversions at 175°C, pH 1.5 in the presence of HCl (▲), H$_2$SO$_4$ (■), H$_3$PO$_4$ (×), maleic acid (＊) and 1-propane sulfonic acid (●).

For all runs, significant amounts of soluble and insoluble humin formation were observed. However the quantification of humins was not possible. Furthermore, formation of insoluble humins precluded performing carbon balances on the samples. Only conversions of monosaccharides and yields of furanic compounds were calculated. When the effect of acid type on the conversion rates was analyzed at pH 1.5 at 160°C (Figure 1), no significant difference was observed in the sugar consumption rate due to the proton source. The chemistry of the monosaccharide conversion is performed via
protons mostly and the effect of dissociated anions could not be observed. Relative activity of the sugars was 8:4:1 for fructose: xylose: glucose.

Figure 2. Glucose conversions at 160°C at pH 3.6 in the presence of HCl (▲), H₂SO₄ (■), H₃PO₄ (×), maleic acid (♦️) and 1-propane sulfonic acid (♦️).

On the other hand, different acids led to different selectivities towards dehydration products for each sugar as shown in Figure 3. For glucose and fructose, the selectivity followed the decreasing order of H₃PO₄, H₂SO₄ and HCl. This trend also follows the order of basic strength. Hence complexion of the dissociated anions with the intermediate leading to HMF formation can be speculated, the strength of which varies according to the base strength of the dissociated anion. Such a complex formation of HMF or its intermediate with Cl⁻ and SO₄²⁻ was mentioned previously when the glucose dehydration in the presence of magnesium and aluminum salts were studied [22]. In that study saturated solutions of salts were used in the absence of acidic protons and the different activities by chlorides and sulfates were explained by sulfates and chlorides constituting different classes of salts exerting different effects on glucose reactivity. Dehydration to HMF proceeds with the participation of aquo- and hydroxyl- complexes
by intermediate consisting of extensively hydrogen-bonded species in the presence of sulfate ions, whereas an exocyclic –CH\textsubscript{2}OH elimination originating from “anions guiding rail” was responsible for the furan ring formation in the presence of chloride ions [23]. The conditions used in this study, e.g. much lower concentrations of anions and presence of acidic protons, did not lead to a discernable difference between the activities of HCl and H\textsubscript{2}SO\textsubscript{4} for glucose consumption. In fact, solutions of sulfuric acid contain bisulfate ions in higher concentrations than the sulfate ions, which are less strong. Thus a better explanation for the higher selectivity with H\textsubscript{2}SO\textsubscript{4} than HCl is the complexation of Cl\textsuperscript{-} anions with the HMF itself causing its further conversion and thereby decreasing the yield [23].

**Figure 3.** HMF selectivity after 30 min at 160 °C in the presence of different acids at pH 1.5 for xylose ( ), glucose ( ), fructose ( ) and at pH 3.6 for glucose ( ).

Although the type of the acid did not affect the monosaccharide conversion rates, the acidic strength affected the glucose conversion rates at pH 3.6 at 160°C (Figure 2). A similar trend was also observed at 145°C at pH 3.6. The conversions in the presence of
maleic acid, phosphoric acid and 1-propanesulfonic acid remained similar to each other, whereas the conversions for hydrochloric acid and sulfuric acid diverged from their activity and constituted a different trend. At 160°C at pH 3.6, the relative rates of the monosaccharides were in the order of 5:3:1 for fructose: xylose: glucose.

A possible explanation of the change in the relative trends can be made by comparing the ongoing reactions driven by the acidity and their rates. Fructose and xylose conversion occur at higher rates than glucose. At such high rates, base catalysis is less powerful on the rate-determining step than is acid catalysis. This statement is also valid at pH 1.5 for glucose; the high proton concentration shields the base catalysis effect of the dissociated anion. At pH 3.6, dissociated anions display their power to catalyze more apparently due to the reduced power of acidic protons. Such a change leads to different mechanisms being dominant at different regimes, which is also pronounced with the activation energies.

For the conversion of monosaccharides, first order reaction kinetics are highly accepted in modeling [5, 8]. In this study, also the Arrhenius equation for the initial first order reaction rates was used (Equation 1).

\[ k = A \times \exp \left( \frac{-E_a}{RT} \right) \]  

(Equation 1)

Activation energy values were found to be in the same order for all the acids with the exception of weak acids at pH 3.6 (Table 2). Under these conditions, activation energy for glucose was much lower than the commonly reported values. That kind of low activation energy was reported in the presence of organic acid functionalized mesoporous silica previously [17]. Also, Mosier’s group reported a similar activation energy in the presence of maleic acid and suggested that different mechanisms were involved in the presence of maleic and sulfuric acids [24], but the conditions which
caused the difference in the mechanism were not explained clearly. It was solely attributed to the enzyme mimicking character of maleic acid that stabilized the glucose. Neither were the details of the mechanism change explained. The presence of different mechanisms was mentioned by Antal et al. also [3], but the conditions leading to their existence were not assigned. Rather, it was mentioned that the second mechanism was going through an activation constant which is similar to the fructose mechanism and was more likely to happen than the other mechanism.

Table 2. Activation energies for glucose, fructose and xylose.

<table>
<thead>
<tr>
<th>Glucose</th>
<th>$E_a$ (kJ/mol)</th>
<th>pH 1.5</th>
<th>pH 3.6</th>
<th>Literature values</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>138</td>
<td>137</td>
<td></td>
<td>1.5M sulfuric acid (4)</td>
<td>137</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>142</td>
<td>138</td>
<td></td>
<td>50 mM sulfuric acid (8)</td>
<td>118</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>145</td>
<td>82</td>
<td></td>
<td>50 mM maleic acid (5)</td>
<td>73</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>138</td>
<td>78</td>
<td></td>
<td>20% SBA-15-BuCOOH (29)</td>
<td>79</td>
</tr>
<tr>
<td>Propanesulfonic acid</td>
<td>148</td>
<td>83</td>
<td></td>
<td>15% SBA-SO$_3$H (29)</td>
<td>75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fructose</th>
<th>$E_a$ (kJ/mol)</th>
<th>pH 1.5</th>
<th>pH 3.6</th>
<th>Literature values</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>132</td>
<td>136</td>
<td></td>
<td>50 mM sulfuric acid (4)</td>
<td>138</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>139</td>
<td>128</td>
<td></td>
<td>1.5 M sulfuric acid (8)</td>
<td>136</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>146</td>
<td>144</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic acid</td>
<td>138</td>
<td>142</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Xylose</th>
<th>$E_a$ (kJ/mol)</th>
<th>pH 1.5</th>
<th>pH 3.6</th>
<th>Literature values</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>133</td>
<td>136</td>
<td></td>
<td>50 mM sulfuric acid (4)</td>
<td>134</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>135</td>
<td>138</td>
<td></td>
<td>1.5M sulfuric acid (8)</td>
<td>134</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>128</td>
<td>126</td>
<td></td>
<td>Hydrothermolysis (37)</td>
<td>137</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>138</td>
<td>150</td>
<td></td>
<td>50 mM maleic acid (38)</td>
<td>204</td>
</tr>
<tr>
<td>Propanesulfonic acid</td>
<td>150</td>
<td>127</td>
<td></td>
<td>15% SBA-SO$_3$H (29)</td>
<td>150</td>
</tr>
</tbody>
</table>
This change in the activation energy was also reflected in the pre-exponential rate constants, which were determined by Arrhenius plot also and are tabulated for glucose in Table 3. Saeman in 1945 [25] has modified the classical Arrhenius equation to predict the effect of proton concentration on cellulose hydrolysis and glucose degradation, where the acid concentration was expressed separately from the pre-exponential factor. This equation was highly accepted and was even further generalized by replacing the acid concentration with proton concentration to produce a modified Saeman equation [5] (Equation 2).

\[
k = A_0 \times [H^+]^m \times \exp\left(-\frac{E_a}{RT}\right)
\]  

(Equation 2)

In this equation a special term m is defined to account for different effects of different acid catalysts or different reaction conditions. In order to determine the constant m, the proton concentration at the reaction temperature has to be known. However the pH changes according to the reaction temperature and the y-intercept of the fitted Arrhenius plot includes an average effect of these altering pH values. Because the determination of constant m was beyond the scope of this study, the pre-exponential factors were determined by using the conventional Arrhenius plot and not the modified Saeman equation. Thus, the proton concentration in included in those rate constants implicitly. This fact does not create a problem when comparing the acids under the same pH. Nevertheless the values were in the same range for all the acids at pH 1.5. However in pH 3.6, there is about 5-6 orders of difference between the weak acids and strong acids.
Table 3. Pre-exponential rate constants for glucose (* Modified Saeman equation constants with the assumption of m equal to 1).

<table>
<thead>
<tr>
<th>Glucose</th>
<th>A (min⁻¹)</th>
<th>A₀ (min⁻¹)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 1.5</td>
<td>pH 3.6</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>5.46E14</td>
<td>4.40E12</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>7.18E14</td>
<td>5.78E12</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>8.15E14</td>
<td>3.57E04</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>8.26E14</td>
<td>3.52E05</td>
</tr>
<tr>
<td>Propanesulfonic acid</td>
<td>6.96E14</td>
<td>4.26E05</td>
</tr>
</tbody>
</table>

In order to compare the pre-exponential factors for different pH values, the factor m in Saeman equation was assumed to be 1, which is a highly accepted value [4], and the modified constants are also listed in Table 3. When the effect of proton concentration was deconvoluted form the pre-exponential rate constant, similar values were obtained for different pH values in the presence of strong acids. However, in the presence of weak acids there still exists a large difference between the constants at pH 1.5 and pH 3.6, also indicating a change in the mechanisms due to pH.

According to one of the proposed mechanisms, the activated transition state in the glucose conversion was believed to involve 1, 2-enediol intermediate and dehydration via further enolization and formation of hexosuloses as represented by the acyclic route in Figure 4. Because the open-chain form was responsible for the formation of the 1, 2-enediol intermediate, the lower activity of glucose was explained by the lower ratio of the open-chain form. Therefore the rate limiting step was proposed to be the protonation of the pyranose form and subsequent ring opening [3].

Alternatively it was suggested that glucose isomerized first to fructose and then followed the same decomposition pathway as fructose [12]. The rate-determining step was believed to be the isomerization, which allows glucose decomposition to have
different activation energy than that of fructose decomposition. Glucose can be isomerized to fructose via base or acid/base catalysis. In fact, base catalysis is much more effective for the isomerization compared to acid catalysis. In the presence of both acid and base, a concerted push-pull mechanism was suggested, that is first driven by the attack of the base. In the presence of the base only, the isomerization took place via a hydride shift from C2 to C1 and formation of 1, 2-enediol intermediate was not observed [19].

Studies simulating the xylose and glucose degradation pathways [7, 27, 28] revealed that different mechanisms can dominate depending on the reaction conditions, such as the acidity, presence of co-solvents, or the temperature; but the protonation of glucose molecule is the rate limiting step nevertheless. While the strongest proton affinity was shown by the C2-OH group and only the protonation of this group leads to the formation of HMF both in vacuum and in studies with explicit water molecules, the protonation of C3-OH group may or may not take place depending on the acidity. At lower acidities usually the proton at C3 transfers back to water molecule, while at higher acidities this protonation may lead to degradation [27]. In that case, ring opening was observed following protonation. On the other hand, the protonation at the C2 resulted in the formation of 2, 5-anhydride ketose intermediates directly via a hydride shift [27]. Subsequent elimination of water molecules from the 2, 5-anhydride intermediate occurs readily similar to fructose degradation, as represented by the cyclic route in Figure 4.

Mechanistic study of fructose dehydration to HMF at 250ºC with 50mM sulfuric acid revealed that the formation occurs via fructofuranosyl-cationic intermediate rather than 3-deoxyhexosulose intermediate via enediol reactions [6]. Only under weak acidic conditions some formation of HMF from fructose via 3-deoxyhexuloses was observed at rates relatively slower than the other mechanism. This mechanism that was originally
proposed by Antal and Mok [6] was accepted in the later studies at varying acidic
conditions and temperatures as well. In our study, the observed activation energy was in
good agreement with the previously reported values and did not change according to the
acidic strength or the pH. Hence the proposed mechanism, shown in Figure 5, was also
accepted to explain the findings of this study.

Further insight is provided by xylose degradation mechanisms, because xylose is an
aldose just like glucose, but has higher ratio of β-furanose like fructose. Mechanistic
study on furfural formation from xylose revealed that at high temperature acidic regime
xylose is initially present at three different forms [26]. The open-chain form of xylose is
responsible for fragmentation product formation, and the xylopyranose form leads to
furfural via 2, 5-anhydride intermediates, while furanose form is stable [3]. The ring
opening- isomerization was reported to be relatively low at 250ºC in the presence of 10⁻³-
⁻² M H₂SO₄. The different pathways for xylose decomposition are summarized in
Figure 6.

A mechanism change was not observed in our study according to the acidic strength
or pH and our values were consistent with the literature values, but such a change was
observed in the xylose degradation during the hemicellulose hydrolysis in the presence
of maleic acid [18]. A further change in the examined pH and temperature regimes may
lead to such a change.
Figure 4. Glucose decomposition mechanisms (decomposition via fructose isomerization (○); acyclic route (□); cyclic route (△)).
Figure 5. Fructose dehydration mechanism.
Figure 6. Xylose decomposition pathways.

Considering the different pathways for xylose and the HMF formation mechanism from fructose, it seems more likely for glucose to isomerize first to fructose and then decompose like fructose at lower pH values, whereas at 3.6 in the presence of weak acids it decomposes directly from the 1,2-enediol intermediate. It is also possible that the cyclic route is followed at higher pH values. Base on the experiments on this study, establishing a further relationship between the observed activation energies and the decomposition mechanisms is not possible. However, competitions existing between the
water molecules as weak bases and the hydroxyl groups of the monosaccharide molecules were believed to have a strong effect on the monosaccharide conversion pathways [7, 27, 28]. In fact, due to higher proton affinity of glucose compared to xylose, this effect is more pronounced on glucose as compared to xylose. On the other hand, at higher acidities where protonation may not be the rate limiting step hydrogen-bonding interactions between the solvent water molecules and the sugar ring could alter the reaction pathway by upsetting the relative stability of the C-C and C-O bonds [28].

**Conclusions**

Understanding the degradation pathways of monosaccharides and the effect of acidic properties on them is of great importance for optimizing both the polysaccharide hydrolysis and the monosaccharide dehydration. Regardless of the nature of the acid, only H⁺ activity is responsible for the degradation rates of fructose and glucose, while the dissociated anions leads to differences in selectivity towards HMF and furfural. The strength of the acid affects the main mechanism for glucose degradation. In the presence of weak homogeneous acids, glucose undergoes degradation through different mechanisms at pH 1.5 and at pH 3.6. Such a mechanism change does not occur in the presence of strong homogenous acids. Fructose and xylose undergo degradation via a single mechanism regardless of the pH and nature of the homogeneous acid. A common framework bringing systematic data together provided insight about the effect of the acid on monosaccharide degradation and enabled design of heterogeneous catalysts for the dehydration of monosaccharide into furanic compounds that are versatile building blocks for the polymer industry.
References

CHAPTER 5. HIGHLY EFFICIENT HYDROXYMETHYL FURFURAL PRODUCTION FROM GLUCOSE

A paper to be submitted to Journal of Catalysis

Basak Cinlar¹, Yomaira Pagan-Torres², James A. Dumesic², Brent H. Shanks¹

¹ Chemical and Biological Engineering Department, Iowa State University
² Chemical and Biological Engineering Department, University of Wisconsin-Madison

Authorship roles:

Cinlar: Primary author, designed and conducted the experiments
Pagan-Torres: Second author, participated in the design of experiments
Dumesic, Shanks: Principal investigators

Abstract

Production of hydroxymethyl furfural (HMF) from glucose or its polysaccharides in a highly efficient manner presents a barrier for the integration of biorenewables technologies into chemical industry. Recently, ionic liquids were found to be active catalysts for the conversion of glucose into HMF, but these processes are not likely to be commercialized due to the industrial difficulties in handling ionic liquids. Similar improvements in the yields can be achieved by using electrolyte solutions under pressure. In this study, chloride salts, such as NaCl, MgCl₂ and AlCl₃, were used to produce HMF from glucose under mild pressures in the presence of hydrochloric acid. HMF yields of ca. 25% were obtained in 30 mins at 160°C in the presence of 0.8M MgCl₂ solution at pH 1.5. Further improvement was achieved by the addition of an organic phase to extract HMF that led to HMF yields up to 57%. In this study we
represent the enhancement in the glucose conversion and HMF selectivity due to the combined effect of salt solution, pressure and acid catalyst and investigate the role of each element in the reaction. By further shortening of reaction time and elevated pressure, the described process has promising potential for converting glucose into HMF very efficiently.

**Introduction**

Facile commercial production of versatile polyfunctional compounds from biomass constitutes a great challenge for establishing a sustainable chemical industry. One such important example is production of hydroxymethyl furfural (HMF) from biomass that has been identified as one of the primary building block chemicals due to its potential to substitute terephthalates in polymer industry [1]. Considerable effort has been put in developing an industrially feasible process for its production via dehydration of hexoses. However, its massive production is still hindered by several reasons, one being the use of fructose as feedstock, which contributes to high production cost due to its lower abundance and thus higher price for large scale production. For its higher abundance, glucose is a cheaper alternative; however its stable structure does not allow its utilization for feasible HMF production [2]. There are no known commercial processes developed for the production of HMF from glucose yet. In this study, an acid catalyzed method involving glucose complexation with alkaline earth metal salts under mild pressure is proposed to produce HMF with high efficiency.

Most of the recent efforts dedicated to HMF production have acquired one of the following two strategies, combining isomerization of glucose to fructose with subsequent dehydration of fructose or employing metal complexes to activate the glucose ring selectively for the formation of HMF intermediate. In the former approach,
acid and bases need to be used in concert because isomerization is a base- and dehydration is an acid-catalyzed reaction. This adds complexity to the entire process. In the latter approach, complexation of glucose with metals, such as copper or chromium in the presence of ionic liquids has shown to activate the ring for selective HMF production. The fact that highest reported HMF yields, ca. 70%, were achieved by using ChCl$_3$ in methyl imidazolium chloride [2] made ionic liquids a popular choice and the focus of several recent studies [3-10]. However, processes involving ionic liquids do not offer industrially viable solutions due to high production costs of ionic liquids and laborious treatment requirements.

The underlying reason for the good activity in the presence of ionic liquids can be explained in terms of their ability to form complexes with glucose, activate the ring, and hold the molecule in a particular orientation so that it undergoes selective dehydration. The internal structure of the ionic liquids also helps in stabilizing the transition state. Alternatively, if the same effect can be achieved with complexation agents in water, the disadvantages of ionic liquids can be avoided [3, 4].

Complexation of electrophiles with glucose was first reported for its isomerization to fructose, where aluminum hydroxide was found to be an effective catalyst by forming a tridentate complex [11]. A similar complexation of Ca$^{2+}$ ions with the glucose unit of cellulose was also observed when the effect of minerals was investigated for the thermopyrolysis of biomass [12]. Significant amounts of HMF were observed among the pyrolysis products. The effect of alkali and alkaline earth metal salts were also examined for the dehydration of glucose and fructose [13, 14]. While the addition of NaCl, CaCl$_2$ and MgCl$_2$ did not improve the HMF yields from fructose significantly, their saturated solutions resulted in improved yields from glucose.
The role of this complexation has been explained by binding of the cations to glucose and supplying water molecules to the positively charged molecule in the proper direction for dehydration to occur [14]. Whether the anion plays a role in this mechanism depends on the type of the anion. For chlorides, it was suggested that the Cl\(^-\) binds to the H\(^+\)'s of the hydroxyl groups, that increases the electron density of the O’s and thereby facilitates the complexation of Mg\(^{2+}\) and Ca\(^{2+}\) with the glucose molecule. Such ‘anion guiding rail mechanism’ was not observed for NO\(_3^-\) due to the bulkier structure of the group [15]. Also sulfate salts did not play a significant role in the complexation process. Rather, the complex was predicted to involve aquo- and hydroxyl groups of water excessively [13]. Based on these studies, it can be deduced that water does not only serve as a solvent in the presence of alkali and alkaline earth metal salts, but also plays an effective role in the formation and stabilization of the transition state.

Similarly water was also suggested to participate in the transition state during the mutarotation of glucose [16]. The negative activated volumes were used to explain the importance of internal water structure on the rates. It has been reported that the internal structure of water can be modified by applying pressure. The rates of mutarotation were found to be higher when pressure was applied to the reaction system [17-19]. In the presence of acids, dehydration and mutarotation, both share a common rate limiting step, which is the protonation of C2-OH [17, 20]. If these two reactions were also to share a similar transition state, it can be speculated that a change in the internal water structure by applying pressure will improve the dehydration yields as well.

The effect of pressure on dehydration rates has not been not thoroughly investigated, but glucose decomposition in sub- and supercritical water has been studied [21-25]. The results have indicated positive effects of water structure on the decomposition rates under those conditions. These extreme conditions that are necessary for improved rates...
in the presence of pure water may not be necessary in the presence of acid and salts, because the salts readily modify the internal water structure and catalysis is performed by the acid instead of water.

By combining the acid catalysis with complexation by salts and rearranging the internal water structure via pressure application, we report a highly efficient method for the production of HMF from glucose in this study. The HMF yields were further improved by using an organic layer to extract HMF and thereby preventing its further conversion. Overall, the unprecedented method proposed in this study delivers HMF with compatible yields to that was obtained in the presence of ionic liquids under industrially feasible conditions and therefore promises high potential for commercialization by further optimization.

**Experimental**

Hydrochloric acid (12N, Fisher) as catalyst, the substrates glucose (99%, Fisher), and cellobiose (98%, Fluka), and the complexation salts, sodium chloride (99%, Fisher), potassium chloride (99%, Fisher), magnesium chloride hexahydrate (99%, Fisher), calcium chloride dihydrate (99%, Sigma-Aldrich), aluminum chloride hexahydrate (99%, Fluka), potassium sulfate (99%, Fisher), aluminum sulfate (99%, Fisher), calcium sulfate (99%, Sigma-Aldrich), and calcium phosphate (99%, Fluka) were used as purchased without further purification. The starch used as another substrate was provided by Grain Processing Company.

In order to prepare the glucose feed solution, hydrochloric acid was added into nanopure water until a pH value of 1.5 was reached. The pH value of the solution was measured by combined glass electrode (6.0233.100, Metrohm) attached to Metrohm 798 MPT Titrino automatic titrator. Before each measurement the electrode is calibrated
using three standard buffers at 4.00, 7.00 and 10.00. Corresponding amount of glucose was added followed by the addition of salt. Finally, extra glucose was added to adjust the glucose content to 5 wt%. For the experiments run with starch and cellobiose, the feed solutions were prepared in a similar manner. In the preparation of organic phase, methyl-isobutyl ketone (MIBK) was mixed with 2-butanol in the ratio of 7:3 (w:w). For the biphasic systems, the ratio of aqueous phase to organic phase was 1:2 (w:w).

Kinetic experiments under 150, 250 and 350 psig pressure were performed at 160°C in a 50 ml stirred batch reactor (Parr Assoc.) under vigorous stirring, ca. 600 rpm. Temperature control was maintained with a PID controller attached to heating jacket. The feed solution, either alone or together with the organic phase, was charged to the reactor before heating was started. The pressure was applied after purging the air inside several times. The heating period took about 10-11mins and time zero was taken as the time when the desired reaction temperature was reached. Data were collected either during the run via a sampling port or at the end of kinetic run after subsequent cooling to 33°C in 5-6 mins. As initial screening, the effect of mixing on the mass transfer limitations was investigated and 600 rpm was found to be sufficient to overcome those. Also the effect of in situ sampling on the reaction kinetics was investigated and no change due to the sampling during the run was observed.

Kinetic experiments under pressures higher than 350 psig were performed in 250 ml stirred batch reactor (Autoclave Engineers) under vigorous stirring, ca. 1700 rpm. A similar procedure to the procedure described above was followed. The monophasic run with 0.8 M MgCl₂ under 350 psig resulted in the same results in both reactors. However the kinetic runs under autonomous pressure did not result in reliable data in these reactors due to the high amount of water in the vapor phase increasing the glucose concentration in liquid phase. Instead, 10 ml thick wall glass tube reactors were used to
generate data under autonomous pressure. In this case, the glass reactor was immersed to preheated oil bath at 160°C. It took about 8 mins to reach the reaction temperature back that decreased with the immersion of glass reactor. The temperature inside the glass reactors was assumed to be same as the temperature of the oil bath.

Samples that were collected during the kinetic runs were filtered through 0.2µm nylon filter (Cobert Assoc.) and diluted 100 times prior to HPLC analysis. The samples were analyzed with Hi-Plex H+ column (Polymer Lab.) at 65°C on a Waters HPLC system equipped with Waters 2414 Refractive Index detector (RID) at 50°C and Waters 996 Photoiodide Array Detector (PAD). The mobile phase was 10mM sulfuric acid solution flowing at 0.6ml/min. While the RID peak areas of the non-diluted samples were used to estimate the sugar concentration, HMF concentrations were determined using the PAD peak areas at 280 nm for the diluted samples. Both the RID and the PAD peak areas were calibrated using 5 different standard solutions for glucose and HMF prior to analysis and a linear relationship of the peak area with the concentration was assured.

Results and Discussion

The effect of salts on glucose conversion was demonstrated with addition of 0.8 M Group I- III chlorides into 5 wt% glucose solution of pH 1.5 at 160 °C under 350 psig N₂ pressure and the results are shown in Figure 1-a. All chloride salts improved the glucose conversion when compared to the HCl alone, in fact almost half of the glucose was already converted before the desired reaction temperature was reached in the presence of alkaline earth and aluminum cations. This improvement in the glucose conversion was also reflected in the HMF yields, as shown in Figure 1-b. As compared to the 3% yield in the presence of HCl only, the yields increased up to 25% with the
addition of alkaline earth metal chloride salts. Alkaline earth metal salts showed higher activity than the alkali salts. Among the alkaline earth metals salts, the activity of MgCl$_2$ was slightly better than that of CaCl$_2$.

**Figure 1.** Glucose conversions (a) and HMF yields (b) in the presence of 0.8 M salt solutions (HCl only (□), NaCl (○), KCl (△), MgCl$_2$ (▽), CaCl$_2$ (+), AlCl$_3$ (◇)).
Complexation of alkali and alkaline earth cations with carbohydrates was reported previously [13, 14]. While the presence of salts did not lead to significant improvement in the fructose decomposition, glucose decomposition rates were accelerated in the presence of alkaline earth metals. Among the alkaline earth metals, Ca$^{2+}$ was found to be more selective towards HMF while Mg$^{2+}$ showed higher selectivity towards levulinic acid, one of the degradation products of HMF, when the saturated solutions of MgCl$_2$ and CaCl$_2$ were tested for their ability to glucose decomposition [13]. Considering high concentration of salts in saturated solutions, referring ca. 7 M, it can be expected that higher activity of MgCl$_2$ leads to HMF degradation readily and produces levulinic acid, whereas HMF degradation occurs to a small extent at lower concentrations of MgCl$_2$ like in our study. The slightly better activity of Mg$^{2+}$ in this study may point out its stronger complexation ability as compared to Ca$^{2+}$ that turns out to be a disadvantage at higher concentrations by leading to further reaction of HMF.

AlCl$_3$ addition increased the glucose conversion rate even more effectively than the alkaline earth cations as shown in Figure 1-a. However it caused to HMF degradation readily, thus the overall HMF yield was not as high for the Al$^{3+}$ as it were with the Mg$^{2+}$ and Ca$^{2+}$ (Figure 1-b). In a study where the effect of aluminum hydroxide as catalyst was investigated for the isomerization of glucose into fructose, a tridentate complex involving C-1, C-3 and C-4 hydroxyl groups of glucose was mentioned to account for the rate enhancement [11]. As counter to that tridentate complex, alkaline earth metal cations are able to form bidentate complexes involving C-1 and C-3 [12]. The faster decomposition rates with AlCl$_3$ compared to MgCl$_2$ and CaCl$_2$ can be related to the formation of different complexes.

Due to its promising potential with high rates at 160°C, the effect of AlCl$_3$ was further investigated at a lower temperature, 145°C, and its activity was compared to that
of chromium chloride and cupric chloride, which were showed to lead enhanced HMF yields with ionic liquids [2]. Figure 2 shows that Cr$^{3+}$, Cu$^{3+}$, and Al$^{3+}$ acted similar to each other, showing no discernable difference in glucose conversions or in HMF selectivity. In another study, where the effect of Group III elements on glucose dehydration was investigated, it was found that all Group III ions were acting similar to each other also, suggesting that the charge of the cation is the key for the improvement [26].

![Figure 2](image)

**Figure 2.** Glucose conversions at 145°C in the presence of 0.8 M AlCl$_3$ (⋄), CuCl$_3$ (○) and ChCl$_3$ (*).

As the results indicate in Figure 2, lower temperatures enabled to capture the conversion kinetics better, but even at lower conversions of glucose, significant amount of HMF loss via further conversion was noticed. Operating at a lower temperature decreased the selectivity towards HMF because of the elongated resident time of HMF in the reaction phase. In search for the existence of a HMF yield regime with AlCl$_3$, the
kinetics was further examined at lower concentrations and summarized in Figure 3. Changing the concentration decreased the conversion and increased the selectivity as expected, but in each case the maximum achieved HMF yield was limited to 25%, which was also the limit reached with MgCl$_2$ and CaCl$_2$.

![Figure 3](image-url)

**Figure 3.** Change in the glucose conversion (□) and HMF yield (■) with the AlCl$_3$ concentration after 20 mins at 160°C.

After the addition of salts, different final pH values were measured for the glucose feed solutions. Although alkali cations did not change the final pH of the HCl solution significantly and 1.45 and 1.49 was measured as the final pH values in the presence of 0.8M NaCl and KCl respectively, MgCl$_2$ and CaCl$_2$ had a larger impact on the final pH value due to the higher ionic strength of the final solution. In their presence, the final pH dropped to 1.2. Having the highest ionic strength, the 0.8M AlCl$_3$ solution had the lowest pH, i.e. 0.8. Hence, the overall proton activity in the pH differed according to the type of salt added although all of the solutions contained the same concentration of acid.
The dehydration of glucose to HMF was reported to be dependent on the available protons previously [24], but it is elusive whether it is the actual proton concentration or the overall proton activity that affects the conversion rates. Because most of the previous studies were conducted at low ionic strength, the proton concentration could be assumed to be equal to the proton activity that was expressed by the measured pH value. Therefore, previous studies reported rate expressions based on pH or proton concentration disregarding the difference between these two terms. On the other hand, at high ionic strengths in this study, the activity coefficient deviates from unity and the measured pH value does not translate to the proton concentration directly. In order to test whether the overall proton activity or the proton concentration affects the glucose conversion, the effect of salt addition on glucose conversion was tested at the same final pH value (i.e. 1.2) and some of the results are shown in Table 1.

**Table 1.** Comparison of glucose conversion (%) and HMF yield (%) after 30 mins in the presence of 0.8M electrolyte solutions under the same pH value.

<table>
<thead>
<tr>
<th></th>
<th>pH adjustment to 1.2</th>
<th>no pH adjustment</th>
<th>Conversion %</th>
<th>HMF yield %</th>
<th>Conversion %</th>
<th>HMF yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl only</td>
<td>14</td>
<td>1.5</td>
<td>8</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>55</td>
<td>18</td>
<td>26</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgCl₂</td>
<td>72</td>
<td>24</td>
<td>70</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlCl₃</td>
<td>89</td>
<td>10</td>
<td>94</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Even at the same pH value, the glucose conversion followed the same trend as in Figure 1, and lower conversions were observed with the NaCl and KCl compared to the other salts. Also, increasing the final pH value from 0.8 to 1.2 did not change the performance of Al³⁺ ions and they were still the most active. As the addition of extra HCl to bring the pH down to 1.2 was not sufficient to equalize the decomposition rates
in the presence of Group I and Group II salts, the decreased proton concentration in the case of AlCl₃ did not diminished its better rate enhancing effect compared to other salts either. In fact, the change in the activity of Al³⁺ ions due to pH change was noticeably less than that of the Na⁺ ions. For further speculation about the role of the proton, the activity of MgCl₂ and AlCl₃ were tested at a final pH value of 2.0. As can be seen in Table 2, again the change in the activity of AlCl₃ according to pH was less than that of MgCl₂ indicating that the effect of proton on the rates changes according to the type of cation.

Table 2. Effect of pH on glucose conversion (%) and HMF yield (%) after 30 mins in the presence of 0.8M electrolyte solutions.

<table>
<thead>
<tr>
<th></th>
<th>pH adjustment to 2.0</th>
<th>pH adjustment to 1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion</td>
<td>HMF yield</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>56</td>
<td>11</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>84</td>
<td>9</td>
</tr>
</tbody>
</table>

Overall, comparing the conversions with and without pH adjustment, it can be suggested that the rate limiting step for the glucose conversion involves the participation of the proton, but it does not account for the overall enhancement solely. The fact that the trend among the cations was preserved under the same pH value and the low conversions in the absence of salts regardless of the pH indicated the crucial role of the electrolytes in the glucose activation. Moreover, the HMF selectivity differed according to the pH values of the solutions indicating the role of proton in the formation of HMF. Similar dependency of HMF selectivity on pH was observed when the effect of pH on HMF selectivity was explored for fructose as well.

An explicit indication of the active role of cation glucose cation complexation in the HMF formation can be obtained by examining the effect of salt at varying
concentrations on the glucose conversion and HMF yields. The values obtained at varying MgCl₂ concentrations are tabulated in Table 3. The 5 wt% glucose feed solution corresponds to 0.2 M, thus both lower and higher Glucose/Salt concentration ratios than 1 were examined. An enhancement was observed with the increasing salt concentration for glucose conversions which was also reflected in the HMF yields. In literature, saturated magnesium and calcium salts were studied for their effect on glucose dehydration [13]. It was claimed that the saturated solutions constitute a different class than the salt solutions at lower concentrations in terms of their complexation abilities. For comparison, saturated magnesium chloride solution was tested for glucose dehydration in this study also. The final pH of the solution was measured as -0.55 and the run was performed at 145°C for 15 min in order to capture the glucose dehydration kinetics. The conversion of the glucose and the yield of the HMF were found to be 78 and 34 % respectively.

**Table 3.** Effect of MgCl₂ concentration on glucose conversion, and HMF yield and selectivity after 30 mins at 160°C.

<table>
<thead>
<tr>
<th>MgCl₂ conc. (M)</th>
<th>pH</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.49</td>
<td>23</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>0.1</td>
<td>1.49</td>
<td>24</td>
<td>8</td>
<td>28</td>
</tr>
<tr>
<td>0.2</td>
<td>1.45</td>
<td>29</td>
<td>9</td>
<td>31</td>
</tr>
<tr>
<td>0.4</td>
<td>1.25</td>
<td>66</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>0.8</td>
<td>1.20</td>
<td>75</td>
<td>24</td>
<td>32</td>
</tr>
</tbody>
</table>

Previously, a concerted mechanism was proposed for the coexistence of acidic protons and magnesium salts, where the concentration of both should were proposed to have an effect on the glucose conversion rates [14]. In that mechanism, no role was assigned to the water molecules in the transition state. Later, this mechanism was modified and the role of complexation is explained not only by increasing the acidity of
the ring and making it more prone to the proton attack but by supplying water molecules at the correct coordination to hydroxyl- groups in order to initiate the conversion. A transition state that involved the free aldehyde form of glucose complexed with cation and water molecules was suggested [14]. Also the studies simulating the glucose and xylose degradation pathways in the presence and absence of water revealed that water plays a significant role in the ongoing mechanism [20, 27].

The internal structure of water is determined by the pH of the reaction media, temperature, the presence of co-solvents, salts and by pressure [20]. Hence a change in any of these parameters will affect the overall HMF yield from glucose if the transition state involves water molecules as suggested. To explore the effect of pressure, the effect of salts was also tested by varying pressure up to 1000 psig. Under autonomous pressure, the conversions and the yields did not show any obvious difference with the type of the salt used and only small amount of enhancement in the HMF yield was observed when compared to HCl without any salt addition, as shown in Figure 4. HMF yields were as low as 1% with 20-30 % conversion and selectivity for MgCl₂ solution. Among the salt solutions studied under autonomous pressure, aluminum chloride showed highest conversion, but the selectivity was rather poor, i.e. about 13 %. At 350 psig, the conversions were significantly higher. Furthermore, an increase in the pressure led to a steady increase in the conversion as shown in Figure 5. Such an enhancement was not observed in the absence of MgCl₂. Application of pressure did not only improve the glucose conversion rates, but improved the HMF selectivity also, indicating the presence of water in the transition state and playing a role in the dehydration step together with the proton and the cation.
Figure 4. Glucose conversions in the presence of 0.8M salt solutions under autonomous pressure (□) and under 350 psig N\textsubscript{2} pressure (■) at 30 mins. (In the case of AlCl\textsubscript{3}, the conversions after 15 mins is shown.)

Figure 5. Effect of pressure (psig) on glucose conversion at 30 min in the absence (□) and presence of 0.8 MgCl\textsubscript{2} (■) at 160°C (HMF yields are shown with (□) on the glucose conversions for MgCl\textsubscript{2} solution).
A similar transition state was reported for the acid-catalyzed mutarotation of glucose from $\alpha$-pyranose to $\beta$-pyranose or from pyranose to furanose configurations [17-19]. For the transition state of glucose mutarotation a negative transition state volume of about $-10 \text{ cm}^3$ was reported and 2 water molecules per glucose molecule were thought to be involved with the transition state. Therefore the rate of mutarotation could be altered easily by changing the internal water structure via addition of co-solvents or application of pressure [17].

The pressures used in this study are not even close to be as high as the applied pressures in those studies and it was surprising that the improved effect could be observed even with a pressure increase as low as 70 bars. Therefore, the inertness of nitrogen pressure was further confirmed by changing the delivery gas to helium. The results under the helium pressure did not show any difference and were able to duplicate the results obtained under nitrogen pressure. Besides, even the air pressure was reported to be inert for the glucose degradation. It can be speculated that the presence of salts contributed to the effect of pressure and the pressure application together with the salts created a synergetic effect on improving the glucose conversion and HMF yields. The depressing effect of salt addition on water vapor pressure is well known. For the depressed vapor pressures by the presence of electrolytes, a pressure application of 70 bars can be more significant than it is for the normal vapor pressures obtained by water solely. The fact that the same rate increase was not observed in the absence of electrolytes further supports the hypothesis. However further clarification on the role of pressure will be considered in future.

About the participation of anions in the glucose complex with cations and water molecules, different theories were proposed. In this study the effect of the anion was investigated by sulfate and phosphate salts at varying concentrations and the results are
shown in Table 4. The effect of Ca(SO₄) was compared to CaCl₂ at two different concentrations ensuring that the activities were compared both at the same cation and anion concentration. In both cases, the activity of Ca(SO₄) was lower than the CaCl₂. Furthermore, runs with Ca(SO₄) and Ca₃(PO₄)₂ were repeated after adjusting the final to 1.2 which was the pH value in the presence of CaCl₂. The trend followed the decreasing order of CaCl₂ > Ca(SO₄) > Ca₃(PO₄)₂. To eliminate the possibility that the anion effect was shielded by the enhancing effect of Ca²⁺, the activity of sulfate ions was compared to chloride ions with their potassium salts. Still the KCl showed lower activity than K₂SO₄. In addition, Al₂(SO₄)₃ was also compared to AlCl₃, but at much lower molarities than the above mentioned salts. In all cases, the activity with the chloride ions was found to be highest followed by sulfate and phosphate ions. Also the HMF yield obtained by chloride anions was higher than the other anions.

**Table 4.** Effect of anion on glucose conversion and HMF yield and selectivity after 30 mins at 160°C under 350 psig N₂ pressure. (* The final pH of the solution adjusted to 1.2)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>0.8</td>
<td>69</td>
<td>37</td>
</tr>
<tr>
<td>Ca(SO₄)</td>
<td>0.8</td>
<td>51</td>
<td>21</td>
</tr>
<tr>
<td>Ca(SO₄)</td>
<td>0.4</td>
<td>49</td>
<td>17</td>
</tr>
<tr>
<td>Ca(SO₄)*</td>
<td>0.8</td>
<td>49</td>
<td>17</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>0.8</td>
<td>33</td>
<td>22</td>
</tr>
<tr>
<td>KCl</td>
<td>0.8</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.8</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.4</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>0.05</td>
<td>85</td>
<td>21</td>
</tr>
</tbody>
</table>

Regarding the effect of anions in the complexation, the chloride ions were reported to be involved with the complex by withdrawing the protons on the hydroxyl groups
increasing the electron density on the oxygens. With the increased electron density, the oxygen atoms were able to form stronger complexes with the cations leading to a more stable structure [15]. On the other hand, this mechanism was not observed with the sulfate ions and the sulfate ions were proposed not to be involved with the complex structure due to their bulkiness. Instead the complex with the cation in the presence of sulfate salts was mentioned to be formed with the aquo- and hydroxyl- groups of the water, a highly hydrated structure [14]. As a result, decreased glucose conversion rates were reported with the sulfate salts as compared to chloride salts, agreeing with the results of this study. Hence, chloride salts are preferred over sulfate and phosphate salts in the aspect of increased glucose conversion rates. However, complexion of chloride ions with HMF itself was reported also leading to further degradation of HMF. Such a negative effect on the selectivity was not observed with the sulfate anions making sulfate salts a better choice for higher HMF selectivity. Alternatively, advantage can be taken from chlorides for faster glucose conversion and their disadvantage for HMF degradation can be excluded at the same time, if a HMF extracting organic phase is coupled with the aqueous reaction phase.

An organic phase consisting of 7:3 (w: w) MIBK-2-butanol solution was suggested to effectively extract the HMF produced during the fructose dehydration in the presence of HCl [1, 28]. The same organic phase was used in this study to extract HMF and thereby prevent its degradation to soluble and insoluble humins. Based on the results presented in Figure 6, the addition of organic phase in the presence of magnesium salts overcame the most common problem in dehydration reactions that is the decrease of the selectivity with the increasing conversion. In the case of aluminum chloride, the degradation of HMF occurred almost simultaneously during its formation, so that addition of the organic phase did not improve the selectivity as much as it did in the
presence of magnesium salts. In the presence of MgCl₂, ca. 57% of HMF yield referring to ca. 70% selectivity at 80% conversion in 30 min at 160°C was obtained. These values are very close to highest reported values [2], which were obtained in the presence of ionic liquids, substances that are not industrially preferred. In fact, these results were not obtained under the optimized reaction conditions. To demonstrate the enhancing effect of extracting phase, the conditions, i.e. salt molarity and pressure, were chosen for convenience and are subject to further optimization. For example, increase in the salt molarity and pressure, and shortened HMF residence times will lead to further improvement in the yields.

**Figure 6.** Effect of organic layer extraction on glucose conversion (■) and HMF selectivity (□) in the presence of 0.8 M MgCl₂ and MgSO₄ at 30 mins, and in the presence of 0.1 M AlCl₃ at 15 mins at 160°C under 350 psig N₂ pressure.

The proposed method in this study for the HMF production from glucose can be further combined with the polysaccharide hydrolysis. When glucose was replaced with starch or cellobiose in the presence of 0.8M MgCl₂ without organic phase, 25% and
19% of HMF yields at 66% and 57% conversions were obtained for starch and cellobiose respectively. Due to the higher stability of the $\beta$-1,4 linkage compared to $\alpha$-linkages, the activity for the cellobiose was lower than the starch. However, the characteristics of the starch, such as its amylose vs. amylopectin content, degree of polymerization and average chain length may change the hydrolysis rates and therefore the HMF rates. Further investigation of the effect of these characteristics on the HMF yield and the extension of the study for cellulosic compounds are among the further aspects of this study.

**Conclusions**

Presence of salts in the acidic media enhances both the glucose conversion and the selectivity towards HMF via complexation and directing the water molecules to the complex. Due to the role of water in the transition state complex, the change in the water structure affects the glucose conversion and HMF yields, which can be manipulated by applying pressure. The effect of pressure on water structure is sensitive to the presence of electrolytes. Overall, the combined effect of electrolyte solutions, pressure and acid catalyst promise high potential for the efficient HMF production from glucose. Using the same process, hydrolysis of starch products can be combined with the dehydration without any sacrifice in the activity.

**References**


CHAPTER 6. FUTURE CONSIDERATIONS AND GENERAL CONCLUSIONS

Future Considerations

The combination of alkali earth metals, acid catalyst and pressure results in highly improved yields of HMF from glucose. Further improvement is achieved by the integration of an organic layer to extract the formed HMF and prevent its degradation. However, the process is already complicated by the presence of the organic layer and the partition of salts in the organic layer constitutes further complication. The increased separation costs decrease the industrial feasibility of the entire process. A robust heterogeneous catalyst with high density of strong acid sites replacing the hydrochloric acid will cut down the separation costs and environmental hazards. The separation costs can further be reduced if the catalyst is capable of separating the HMF simultaneously from the aqueous reaction media during the reaction.

Most of the highly thermally stable catalysts designed for the gas phase reactions do not perform well in the condensed aqueous phase reactions due to their limited hydrothermal stability. Despite their unique textural and catalytic properties, mesoporous silica catalysts were not good candidates for the dehydration reaction because of the hydrothermal stability problem. Recently, sulfonic acid moieties were incorporated onto activated carbon by a previous group member successfully following the method suggested by Hara et al. The materials showed high hydrothermal stability and competitive catalytic activity to sulfuric acid for the dehydration of fructose, even after hydrothermally treated.

These sulfonated carbon species were prepared by pyrolysis of sucrose to create the active carbon species followed by sulfonation via wet impregnation. To remove the
physisorbed and chemisorbed sulfates the final material were calcined again. The resulting material has a surface area of ca. 0.2 m$^2$/g with a total acid capacity of ca 1.3 meq/g. Although the surface area is rather low for a heterogeneous catalyst, the acid density is within the same range as organic acid functionalized mesoporous silica. In order to test the hydrothermal stability, the catalysts were treated in aqueous phase at 145°C for 2 hrs under 350 psig pressure. These conditions were chosen to mimic the dehydration reaction conditions. After 3 times of hydrothermal treatment, the characterization studies showed that the materials still kept most of their acidic sides, which was also proved by their catalytic activity. The untreated and hydrothermally treated samples were tested for their activity in fructose dehydration. The results are shown in Table 1.

Table 1. The activity of the fructose dehydration to hydroxymethylfurfural at 145 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Fructose wt% ±0.15</th>
<th>HMF wt% ± 0.0</th>
<th>Conversion %</th>
<th>Selectivity %</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC0*</td>
<td>0</td>
<td>4.92</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.19</td>
<td>0.63</td>
<td>35</td>
<td>52</td>
<td>18</td>
</tr>
<tr>
<td>SC3</td>
<td>0</td>
<td>4.67</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.15</td>
<td>0.68</td>
<td>32</td>
<td>73</td>
<td>24</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>0</td>
<td>4.78</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.72</td>
<td>0.48</td>
<td>22</td>
<td>73</td>
<td>16</td>
</tr>
</tbody>
</table>

In these tests the conversion of fructose to HMF was measured at 145°C under 350 psig pressure in the presence of sulfonated carbon catalyst as synthesized, 3 times hydrothermally treated sulfonated carbon catalyst and sulfuric acid. The amount of the catalyst in each batch was adjusted so that the final pH of the solution was the same in each case, i.e. 3.3. As shown in the Table 1, no significant loss in the catalytic activity
was observed due to the hydrothermal treatment. In fact, the catalysts showed competitive active with the sulfuric acid. Hence sulfonated carbon species promise potential as active catalysts for the dehydration. However high yields of HMF from glucose were only observed at very fast reaction rates. With this loading density of acidic groups, it is difficult to reach low pH values required for high yields.

In order to increase the total acid capacity per gram, the spatial density of the acidic groups does not need to be changed. By increasing the surface area, total acid capacity can be increased for the same acidic group density per area. Thus a different support with a higher surface area will resolve the problem. Dispersing the sucrose onto mesoporous silica surface was suggested before to increase the surface area. However the low hydrothermal stability of the mesoporous silica was observed due to the strong interaction of the surface hydroxyl groups with water inducing silica hydrolysis and condensation. Because immersing sucrose on the surface will not cover all of the surface hydroxyl groups and the remaining groups will cause collapse of the entire structure again in the presence of water, immersion of sucrose onto silica is not a feasible option to increase the surface area.

Alternatively, β-cyclodextrin can be used as starting material instead of sucrose. β-cyclodextrin consists of 7 glucose units connected via glycosidic bonds building an inside hydrophobic cavity of 6 Å and has very low water solubility overall. If the cyclic structure can be maintained during the synthesis of the materials, higher surface areas and hence higher total acid capacities per gram can be achieved. While the hydroxyl groups of the glucose units are replaced with the sulfate groups, the glycosidic bonds holding the molecule together has to be preserved. It is not known whether the glycosidic bond linkage in sucrose is preserved during the synthesis. Even if not, there is a higher possibility that glycosidic bonds in the cyclodextrin can be preserved because α
1-4 linkages in the cyclodextrin have higher bond strength compared to the α 1-6 linkage in sucrose. As the catalytically active sites on the final structure will face outwards, the pore size is not important. In deed smaller pore sizes are preferred in terms of increasing the total acid capacity. On the other hand, if bigger pore cavities are desired, recent studies showed that cyclodextrins with larger number of glucose units can be synthesized.

Bigger pore cavities may be useful if a specific product is desired to be trapped in, such as HMF. The hydrophobic character of the cavity can be taken advantage of to extract the HMF from the aqueous reaction layer without using an organic layer. However, in order to take advantage of the hydrophobic character of the cavity, bigger pore sizes may not even be necessary. Due to the low water solubility of β-cyclodextrins, molecules tend to stack on each other forming long hydrophobic channels that can reside multiple HMF molecules. Tests must be run by replacing the organic layer with the β-cyclodextrins to measure its effect on HMF extraction and thereby preventing further degradation of HMF before searching for cyclodextrins of higher orders.

Another point of interest for improving the process further is combining the polysaccharide hydrolysis with the glucose dehydration in one pot. Primary results regarding this has showed that breakage of the β 1-4 linkage in cellobiose represents more of a barrier than α linkages in the starch. Clearly, the characteristics of starch, such as its amylose/amylopectin ratio, degree of polymerization and degree of branching are important parameters affecting the hydrolysis rate. Detailed investigation of the effect of these characteristics on the hydrolysis rate is crucial for the coupling of hydrolysis with dehydration reaction. However under the proper circumstances starch hydrolysis can be combined with dehydration with no sacrifice on the HMF yields. On the hand,
hydrolysis of cellulosic compounds is more troublesome and its combination with dehydration may result in decreased HMF yields according to the primary results. The extent of hydrolysis rates affecting the dehydration must be investigated in a detailed manner. However the process shows potential for one pot synthesis of HMF either from starch or from cellulosic compounds.

**General Conclusions**

Furfural and its derivative, hydroxymethylfurfural (HMF), are important versatile polyfunctional compounds in the polymer industry. Highly efficient industrial production of these materials has gained significant importance due the increasing concerns for a sustainable economy in the shortage of petroleum supplies. While furfural and HMF are produced by the dehydration of the pentoses and hexoses respectively, accompany of many other side reactions decrease the overall product yields. Different mechanisms were suggested for the decomposition of monosaccharides, dominance of which is determined according to the reaction conditions. In the presence of weak acids, glucose decomposes via different mechanisms at different pH regimes. Although low acidic concentration lead to higher selectivity toward hydroxymethylfurfural, slow reaction rates does not allow for development of a viable process under these conditions. At higher acid concentrations, addition of alkaline earth metals under mild pressure increases the glucose ring activity selectively for hydroxyl methyl furfural production. Coupling dehydration with the polysaccharide hydrolysis does not affect the HMF yields and allow for one pot synthesis of hydroxymethylfurfural from starch. These conditions with extraction of hydroxymethylfurfural to an organic layer leads to high product yields that are competitive with the highest yields reported so far for the hydroxymethyl furfural
production form glucose. By further optimization of the parameters, the process promises high potential for commercialization. Substitution of homogeneous acid catalyst with a robust heterogeneous catalyst presents an important barrier for the commercialization. Different acid moieties incorporated into mesoporous silica provide enhanced acidic strength due to the interaction between the acidic groups and are able to display their own strength in water. In terms of understanding the relationship of the functional groups and the support with water, quantum chemical simulations coupled with Monte Carlo method provide a useful tool. Together with the tunable textural properties, organic acid functionalized mesoporous silica materials can be promising for the dehydration if hydrothermal stability is provided. Replacing the mesoporous silica support with the activated carbon provides hydrothermal stability and the catalysts showed activity for the dehydration of fructose. However the catalyst suffers from low surface area and low acid group density. The textural and catalytic properties of the materials need to be improved for their utilization in the dehydration of carbohydrates. Overall, a robust heterogeneous catalyst with sufficient acid catalytic sites can provide high yields of HMF from glucose in the aqueous solution of alkaline earth metals under pressure.
APPENDIX 1. MONOSACCHARIDE DEHYDRATION USING ORGANIC-INORGANIC HYBRID MESOPOROUS SILICA

Abstract

Dehydration of monosaccharides is an important reaction that produces the valuable chemical building blocks in polymer industry, hydroxymethyl furfural and furfural, and is an intermediate step to produce liquid fuels from biomass. In order to increase the feasibility of production of these chemicals industrially, there is a great desire to design an environment friendly robust catalyst offering high selectivity and yield. Mesoporous silica functionalized with organic acids is promising due to the combined advantage of high surface area with tailorable textural and catalytic properties. In this work, propyl sulfonic, arene sulfonic, butyl carboxylic and ethyl phosphoric functional groups were incorporated onto SBA-15 type mesoporous silica support and tested for their activity for dehydration of glucose, fructose, xylose and arabinose in aqueous media. The observed activity was independent of the acidic strength of the tethered group onto catalyst surface. Regardless of the catalyst type, the relative activity of substrates was followed the decreasing order of; fructose, arabinose, xylose, and glucose. The calculated activation energy for substrate consumption using kinetic data at 145, 160 and 175°C were 120 and 130 kJ/mol for xylose and fructose, respectively and did not change according to the type of the functional group incorporated. For glucose, two different activation energies, 80 kJ/mol and 120 kJ/mol, were obtained with different functionalized materials. None of the functional groups showed higher selectivity toward the dehydration product than the others. These results can be explained by the poor hydrothermal stability of the materials at the temperatures used in this study.
Introduction

During the transition from a petroleum-based economy to a bio-based economy, dehydration reaction of monosaccharides is considerably important in two aspects: first, it is an intermediate step in producing liquid alkane fuels from cellulosic materials, and second, the furan derivative products of the reaction are important chemicals in polymer industry [1-3]. Being the most common products of biomass hydrolysis [4-8], xylose, arabinose and glucose are the most widely studied substrates for dehydration. On the other hand fructose is a highly considered substrate for the production of hydroxymethyl furfural (HMF) for its higher activity and rather better-understood mechanism as compared to glucose [9-11]. For industrial applications, catalysts providing both environmental and economical benefits ought to be developed for the reaction. Being cheap and environment-friendly, functionalized mesoporous silica catalysts have been used in similar reaction systems [12, 13] and therefore are promising catalysts for dehydration reactions also. In this work, mesoporous silicas with organic acid functional groups of various acid strengths were tested for their ability to dehydrate monosaccharides.

Dehydration reaction proceeds along with some parallel and consecutive side reactions such as isomerization, fragmentation and polymerization [1-3, 14]. Most of these side reactions involve C-C bond breakage that has a bonding energy of ca. 348 kJ/mol. On the other hand, dehydration reactions involve C-O bond breakage, which has a bonding energy of ca. 360 kJ/mol [10, 11]. The similarity between the bonding energies makes it difficult to decouple them from each other. Moreover, both the side reactions and the dehydration reactions are acid-catalyzed and occur at similar rates at similar temperatures creating further challenges for obtaining high yields towards desired products [9, 14].
Quaker Oats process employing concentrated sulfuric acid is most commonly used to produce furfural from pentoses [15]. In literature, other mineral acids besides sulfuric acid, such as hydrochloric acid and phosphoric acid [9, 16-18], as well as some organic acids, such as acetic acid [19], maleic acid, and succinic acid [20, 21], have also been used to study the dehydration of monosaccharides. In general, it was found that the selectivity decreases highly for conversions over 50%. Besides low selectivity with these acids, corrosiveness of mineral acids and high separation cost for catalyst add to the drawbacks.

Enzymes offer higher selectivity than the homogeneous acids. However their high prices and being easily affected by the reaction environment does not satisfy the needs for an industrial application. There has been some work done with zeolite structures by Moreau and his co-workers [22-24] indicating that the selectivity towards dehydration was affected by the shape of the pores. The authors obtained 90-95% selectivity when the conversion was kept as low as 30%. However, the selectivity decreased significantly at higher conversions. They have also found some activity with a sulfonated polymer-resin commercial catalyst [23], but polymer-resin supported materials provide low surface areas limiting their use for liquid phase reactions. By providing a higher surface area with tunable pore sizes, micelle-templated mesoporous silica has attracted attention as heterogeneous catalysts.

Mesoporous silica functionalized with a wide range of acidic and basic functional groups have been found to be effective for various organic reactions [25]. Recently Dias and the coworkers studied dehydration reaction with MCM-41 type mesoporous silica functionalized with various groups by grafting, and they have found promising results [26-29]. When grafted, the functional groups are not uniformly distributed inside the pores but rather tend to accumulate at the pore openings [25, 30]. One-pot synthesis
method provides a more uniform distribution of the functional groups and thereby offers enhanced reproducibility [30-32]. On the other hand, SBA-n type supports provide higher stability due to its thicker walls compared to MCM-41 [32]. Thus organic acid functional groups tethered onto SBA-15 support are promising heterogeneous catalysts for dehydration reaction. In this work, mesoporous silica catalysts functionalized with organic groups of different acidic strength were tested for the first time for their activity for dehydration of pentose and hexoses, e.g. xylose, arabinose, glucose and fructose.

**Experimental**

For catalyst synthesis, silica precursor tetraethylorthosilicate (TEOS) (98%, Aldrich), and functional group precursors, 3-cyanopropyltriethoxysilane (CPTES) (98%, Gelest), diethylphosphatoethyltriethoxysilane (DEPTES) (95%, Gelest), 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (CSPTMS) (50% in dichloromethane, Gelest), and (3-mercaptopropyl) trimethoxysilane (MPTMS) (85%, Gelest), were used as purchased. The substrates α-D-glucose (99%, Acros), D-xylose (Acros), D-fructose (Fisher Chemicals) were also used without further purification.

**Catalyst synthesis and characterization**

Propyl sulfonic (-PrSO$_3$H), arene sulfonic (-ArSO$_3$H), butyl carboxylic (-BuCOOH) and ethyl phosphonic (-EtPO$_3$H) functionalized SBA-15 type mesoporous silica catalysts were synthesized using the co-condensation procedure described in literature [13, 30, 31, 33]. The functional group precursor to silica precursor molar ratio was the same for each catalyst, e.g. 15%.

As silica template, 4 g of Pluronic 123 (BASF Co.), a tri-block co-polymer consisting of poly(ethylene oxide)/ poly(propylene oxide)/ poly(ethylene oxide), (EO)$_{20}$(PO)$_{70}$(EO)$_{20}$, was dissolved in 125 ml of 1.9 M aqueous HCl solution. TEOS
(8.2 ml) was introduced into the solution when the temperature reached 40 °C. After a pre-hydrolysis period of 45 min, the functional group precursor was added in a molar ratio of 0.15 relative to the TEOS. For oxidation of the thiol groups in SBA-15-PrSO₃H synthesis, 3 parts hydrogen peroxide (30 wt% aqueous, Fisher) with respect to TEOS was added to the mixture. The resulting mixture was stirred for 20 h and aged for 24 h under static conditions before filtration. The surfactant template was removed by total reflux in ethanol with 0.1 M HCl for 24 h. When synthesizing SBA-15-BuCOOH, the functional groups were acidified further by refluxing for 24 h in a 50 wt% aqueous H₂SO₄ solution. The catalysts were recovered by filtration, washed multiple times with DI water/ethanol and oven-dried at 80°C.

Textural properties of the catalysts were determined using nitrogen adsorption/desorption isotherms measured at -196°C by a Micromeritics ASAP 2020 system. Prior to measurement the samples were degassed for 5 h at 100°C. The pore volume/ pore size distributions and surface areas were calculated using BJH and BET methods respectively. The incorporation of the functional groups and removal of the surfactant were confirmed by thermogravimetric analysis from 50°C to 650°C with a temperature ramp of 5°C/min and nitrogen purge using Perkin-Elmer TGA7. Potentiometric titration data of ca.0.02 wt% catalyst in 0.01M sodium chloride solution with 0.005 M aqueous sodium hydroxide was used to calculate the total acid capacities and acid dissociation constants for individual catalysts. Titrations were conducted with a Metrohm 798 MPT Titrino automatic titrator equipped with Metrohm combined glass electrode and the results were analyzed using Metrohm Tiamo software and Gran Plot method as described in literature [34]. The results were confirmed with CHNS elemental analysis using a Perkin-Elmer Series II 2400 CHNS analyzer.
Kinetic runs

The kinetic studies for the dehydration reactions of D-fructose, D-glucose, D-xylose and D-arabinose were conducted in an Autoclave Engineers 100 ml stainless steel batch reactor at three different temperatures, 145, 160 and 175°C. The temperature control was maintained with a programmable logic controller connected to both heating jacket and cooling loop. In a typical reaction run, 100 ml of 11mM aqueous sugar solution together with the corresponding amount of catalyst to contain 0.25 mmol of acidic protons was charged into the reactor vessel and heating was started. To ensure condensed phase reaction environment, nitrogen pressure of 300 psig was applied during the runs after purging the air. Time zero was taken as the time when the desired temperature was reached and the conversion at that time was taken to be zero. Samples were taken every 30 min for 2 h and were filtered through 0.2µm nylon filter (Cobert Assoc.) prior to analysis.

Samples were analyzed for their substrate and product concentrations using a 300x7.7 mm PL Hi-Plex H³ column (Polymer Lab.) at 65°C on a Waters HPLC system equipped with Waters 2414 Refractive Index detector (RID) and Waters 996 Photoiodide Array Detector (PAD). The mobile phase was 10mM sulfuric acid solution flowing at 0.6ml/min. The concentrations of sugars were calculated using RID data. Injection of standard sugar solutions showed that the peak intensities were linearly related to sugar concentrations in the range of 0.5 to 2.0 wt%. To remain in the linear correlation regime for products, data from both detectors were used. Concentrations less than 0.25 wt% were calculated from PAD data at 280 nm whereas higher concentrations of products were calculated from RID data.
Results and Discussion

Catalyst characterization

The functional groups incorporated into SBA-15 are shown in Scheme 1. All the functional groups were incorporated such that the functional group precursor to silica precursor ratio is 0.15 that is slightly higher than the commonly used ratio, e.g. 0.10. This is the highest loading that can be incorporated onto SBA-15 structure. Loadings higher than this result in dis-ordering of mesoporous structure [13, 35]. The N$_2$ adsorption-desorption isotherms for these catalysts displayed Type IV hysteresis loops, characteristic for mesoporous materials, suggesting that the current loadings maintained the mesoporous ordered structure. The calculated textural properties of the prepared catalysts are listed in Table 1. The surface areas and pore volumes were within the expected range for mesoporous materials [36, 37]. The sharp peaks indicate narrow pore size distributions. Also, the t-plot analysis showed evidence for the presence of micropores. The micropores in SBA-15 structures are typical and they are thought to be small enough that no functional groups reside in them [36, 37].

\[ \text{Scheme 1. Functional groups incorporated onto mesoporous silica. Propyl sulfonic acid (a); arene sulfonic acid (b); ethyl phosphonic acid (c); butyl carboxylic acid (d).} \]
Table 1. Textural and catalytic properties of the catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (m²/g)</th>
<th>Avg. Pore Size (Å)</th>
<th>Pore Volume (cm³/g)</th>
<th>Elemental Analysis</th>
<th>Total Acid Capacity (meq/g)</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-PrSO₃H</td>
<td>637</td>
<td>55</td>
<td>0.61</td>
<td>C 1.23, H 3.29, S 0.13</td>
<td>1.2</td>
<td>2.62</td>
</tr>
<tr>
<td>SBA-15-ArSO₃H</td>
<td>758</td>
<td>48</td>
<td>0.92</td>
<td>C 0.59, H 2.5, S 0.16</td>
<td>1.13</td>
<td>2.78</td>
</tr>
<tr>
<td>SBA-15-EtPO₃H</td>
<td>625</td>
<td>64</td>
<td>0.82</td>
<td>C 0.41, H 1.64, S ---</td>
<td>0.75</td>
<td>3.56</td>
</tr>
<tr>
<td>SBA-15-BuCOOH</td>
<td>575</td>
<td>72</td>
<td>0.83</td>
<td>C 0.62, H 2.97, S ---</td>
<td>0.7</td>
<td>4.78</td>
</tr>
</tbody>
</table>

The incorporation of the functional groups and the thermal stability of the catalysts were tested with thermogravimetric analysis in the temperature range of 50°C to 650°C. Three main peaks were identified for the catalysts. The first peak is around 100°C, associated with the loss of physisorbed water [36, 37]. The amount of physisorbed water was found to be approximately 10% of the total weight and was almost the same for all catalysts. Around 250-280°C, the remaining surfactant comes off [36, 37]. The presence of remaining surfactant was also confirmed with the elemental analysis results, having higher C/S ratios than the theoretical value. The last peak belongs to the surface silanol decomposition taking place around 600°C [36, 37].

The elemental analysis results showing C and S amounts and the total acid capacities and the acid strength of these functional groups are also listed in Table 1. For SBA-15-PrSO₃H and SBA-15 –ArSO₃H catalysts, the C/S ratio is higher than its theoretical value that is 3 and 9 respectively. This suggests that some of the carbonaceous materials were retained in the samples, probably from residual surfactants and/or unhydrolyzed methoxy, ethoxy groups of the functional group precursors [25, 35, 37]. The molar S amounts for propylsulfonic and arenesulfonic SBA-15’s indicate their total acid capacity and it was calculated to be 1.1 and 1.2 respectively. The sulfur
content of SBA-15-PrSO$_3$H is in good agreement with the molar ratios of the precursor used to synthesize the materials, demonstrating high corporation yield of MPTMS precursor. Also it is in good agreement with total acid capacity calculated from the titration indicating that all of the thiol groups were properly oxidized. The acidic strength of SBA-15-PrSO$_3$H is found to be close to SBA-15-ArSO$_3$H, these being more acidic than the others. However, positive $pK_a$ values do not indicate any leveling effect due to aqueous media [38]. Hence all the acidic groups are able to display their own acidic strength in water.

**Kinetic studies**

Conversion rates of monosaccharides at 145, 160 and 175°C for each catalyst are plotted in Figure 1. Regardless of the catalyst used, the activity of sugars followed the order; fructose $<$ arabinose $<$ xylose $<$ glucose. While fructose was significantly more active than the other substrates, the conversion rates for glucose, xylose and arabinose were similar. The higher activity of fructose and the stability of glucose structure have been reported in literature at several instances [3, 9, 39]. Comparing the activities of pentoses to each other, arabinose is found to be more active than xylose. There are few studies comparing the relative rates of hexoses and pentoses [40-42]. However, similar relative activities were reported previously by our group. Especially the difference in activities between fructose and the others becomes more significant at 175°C. At 175°C, fructose is almost 5 times more active than the others, whereas the rates were almost in the same order of magnitude at 145°C, as can be seen in Figure 1.
In this study the catalysts are tested such that each run contained the same number of acidic sites. So the trend in the rates was expected to follow the trend of the acidic strengths for each sugar. Only, for glucose conversion at 145°C and fructose conversion at 175°C, the rates with different catalysts increase in the order of increasing acidic strength. Otherwise, catalysts with different acidic strength showed similar activity for a particular sugar. Previous studies by our group have also demonstrated that the activity was dependent only on the acidic proton concentration, regardless of the proton source [12]. The fact was explained with the leveling effect in water.

Leveling effect consists of the concept that no stronger acid than hydronium ion can exist in water [38]. Thus any acid that is stronger than hydronium ion is leveled off to the acidity of it. In order leveling effect can take place, the acid must completely dissociate in water. However a good portion of the incorporated functional groups
remain undissociated in water and are able to display their own strength as expressed by the positive $pK_a$ values shown in Table 1.

A better explanation was provided when the catalysts were examined for their hydrothermal stability. Although they showed high thermal stability, the entire structure collapsed in the presence of water at elevated temperatures used in this study. In order to test for the hydrothermal stability, these catalysts were treated in water at 145°C for 2 hrs and tested for their textural and catalytic properties using N$_2$ adsorption-desorption isotherms and potentiometric titration, respectively after catalyst recovery. Type IV hysteresis loops were maintained after the treatment but significant decrease in the surface area was observed indicating collapse of the silica support. Also the pore size distributions were wide including large pore sizes in the order of nanometers. Moreover, potentiometric titration results indicated that there were no acid groups present after the hydrothermal treatment. As a result, in water at elevated temperatures, the acidic groups leached from the support and the support did not maintained its unique textural properties. The poor hydrothermal stability of the catalysts explain the fact that the rates were proportional to the total number of acidic sites and the effect of the different acidic strength of different functional groups could not be observed.

If any of the functional groups were selectively better for HMF formation, that could still be observed even though the catalysts are not hydrothermally stable. The selectivities with different catalysts at 175°C have been plotted against conversion for each sugar in Figure 2. There is no obvious pattern for selectivity with the different functional groups for any of the sugars, the selectivities changed randomly according to the catalyst used, but SBA-15-EtPO$_3$H leads to higher yields for all sugars. A commonly observed problem, which is that the selectivities decrease with the increasing
conversion, was not recognized with the use of mesoporous silica, most probably due to the low conversions.

Figure 2. Selectivity for HMF and furfural for; a) glucose b) xylose c) fructose, at 175°C in the presence of SBA-15-SO$_3$H (■), SBA-15-phSO$_3$H (▲), SBA-15-PO$_3$H (▼), SBA-15-BuCOOH (◆), propylsulfonic acid (x).
Figure 2. (continued) Selectivity for HMF and furfural for; a) glucose b) xylose c) fructose, at 175°C in the presence of SBA-15-SO$_3$H (■), SBA-15-phSO$_3$H (▲), SBA-15-PO$_3$H (▼), SBA-15-BuCOOH (●, propylsulfonic acid (x)).

Data at three different temperatures were used to determine the activation energies and frequency factors for each substrate and catalyst and the values are tabulated in Table 2. For the calculations, first order reaction assumption was applied as suggested and accepted by several authors [20, 21]. Rather than using product appearance rate, reactant disappearance rates were used in calculations to be able to compare with the literature values. Thus, these activation energies and frequency factors are not specific for the dehydration reaction, but reflect overall conversion of the sugars. Activation energies did not change according to the catalyst used, except in the case of glucose. In glucose conversion, the activation energy was found to be 72 kJ/mol and 135 kJ/mol for
SBA-15-BuCOOH and SBA-15-ArSO$_3$H respectively, indicating the presence of two different mechanisms.

**Table 2**: Activation energy and frequency factors for monosaccharide dehydration

<table>
<thead>
<tr>
<th></th>
<th>Arabinose</th>
<th>Xylose</th>
<th>Glucose</th>
<th>Fructose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-BuCOOH</td>
<td>79</td>
<td>74</td>
<td>71</td>
<td>136</td>
</tr>
<tr>
<td>SBA-15-EtPO$_3$H</td>
<td>73</td>
<td>80</td>
<td>85</td>
<td>131</td>
</tr>
<tr>
<td>SBA-15-PrSO$_3$H</td>
<td>80</td>
<td>78</td>
<td>109</td>
<td>136</td>
</tr>
<tr>
<td>SBA-15-ArSO$_3$H</td>
<td>---</td>
<td>82</td>
<td>135</td>
<td>136</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Arabinose</th>
<th>Xylose</th>
<th>Glucose</th>
<th>Fructose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-BuCOOH</td>
<td>8.04E+06</td>
<td>1.86E+06</td>
<td>2.08E+13</td>
<td>1.27E+14</td>
</tr>
<tr>
<td>SBA-15-EtPO$_3$H</td>
<td>2.19E+06</td>
<td>9.24E+06</td>
<td>6.03E+09</td>
<td>4.29E+13</td>
</tr>
<tr>
<td>SBA-15-PrSO$_3$H</td>
<td>1.27E+07</td>
<td>5.33E+06</td>
<td>1.99E+07</td>
<td>1.70E+14</td>
</tr>
<tr>
<td>SBA-15-ArSO$_3$H</td>
<td>---</td>
<td>1.31E+07</td>
<td>5.62E+05</td>
<td>1.98E+14</td>
</tr>
</tbody>
</table>

When the activation energies were compared to the values in literature, the activation energies for fructose were found to be in good agreement. The two different activation energies observed for glucose at different pH values also exist with the use of homogeneous acids. In a study investigating glucose decomposition in the presence of sulfuric acid and maleic acid, different activation energies were found. The activation energies for xylose were also found to be lower than the commonly reported values. However, establishing further parallelism with the literature values and more detailed explanation of the results is futile due to the low hydrothermal stability of the catalysts. Design of a hydrothermally stable heterogeneous catalyst is one of the major challenges for the dehydration of hexoses and pentoses.
Conclusions

Organic acids of different strength were incorporated onto mesoporous silica support and showed activity for dehydration of pentose and hexoses. Regardless of the type of catalyst used, the decreasing order of the reactivity was fructose, arabinose, xylose, and glucose. Reaction rates were found to be independent of the acidic strength of the tethered group, but they were directly correlated to the total number of acidic sites. The observed trend is explained by the poor hydrothermal stability of these catalysts at elevated temperatures. The different activation energies for glucose with different functional groups indicated presence of different decomposition mechanisms.

References


APPENDIX 2. SULFATED ZIRCONIA MODIFIED SBA-15 CATALYSTS FOR CELLOBIOSE HYDROLYSIS

Volkan Degirmenci¹, Basak Cinlar², Aysen Yilmaz³, Rutger A. van Santen⁴,
Brent H. Shanks¹, Emiel J. M. Hensen⁴, Deniz Uner⁵

¹Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey (formerly), Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands (currently)
²Chemical and Biological Engineering Department, Iowa State University
³Department of Chemistry, Middle East Technical University, Ankara Turkey
⁴Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands
⁵Department of Chemical Engineering, Middle East Technical University, Ankara Turkey

Authorship roles:

Degirmenci: Primary author, synthesized and characterized the catalysts.
Cinlar: Secondary author, conducted the kinetic studies.
Yilmaz: Third author, advised in catalyst synthesis.
Van Santen, Shanks, Hensen, and Uner: Principal investigators.

Abstract
Zirconia modified SBA-15 becomes a very active catalyst for the selective hydrolysis of cellobiose to glucose after sulfation. Spectroscopic investigations indicate the presence of Brønsted acid sites similar to those present in conventional sulfated zirconia. The red
shift of about 140 cm\(^{-1}\) upon carbon monoxide adsorption of the isolated silanol band in sulfated catalysts in infrared spectra is higher than in non-sulfated catalysts (\(~100\) cm\(^{-1}\)) and comparable to the shift in conventional sulfated zirconia. The catalytic activity in cellobiose hydrolysis correlates well with results for temperature-programmed decomposition of \(\text{i}-\text{propylamine}\) for a range of sulfated ZrO\(_2\)/SBA-15 catalysts with increasing zirconia loading. A glucose selectivity of 80% during cellobiose hydrolysis at a reaction time of 30 min at 160 °C is obtained. The yield is much higher than that of conventional sulfated zirconia, most probably due to the absence of Lewis acidic Zr\(^{4+}\) sites in the SBA-15 modified sulfated zirconia. The elution of the sulfur species remains the limitation for the application under hydrothermal conditions.

**Introduction**

So far, considerable effort has been dedicated for the economic production of ethanol as it is an excellent alternative transportation fuel and can be blended with gasoline [1, 2]. However, ethanol is currently produced from sugar cane and the starch portion of corn, competing with food production, thus raising ethical concerns [3]. It is also very important to develop technologies for the efficient utilization of cellulose, a major constituent of lignocellulosic agricultural residues, as one of the renewable sources of chemicals [4, 5]. Cellulose is a polymer of glucose monomers connected by \(\beta\)-1,4-glycosidic bonds. It can be hydrolyzed to glucose through enzymatic or acid hydrolysis [6, 7]. The advantage of the enzymatic route is the absence of the degradation products but the reactions proceed rather slowly and separation is cumbersome [8]. Mineral acids can depolymerize cellulose into individual glucose units, accompanied by degradation products such as furfural, hydroxymethylfurfural and tar-like products. These side products are toxic for the microorganisms used for further fermentation of
the glucose product. Recovery of the mineral acids is another challenge and in any case mineral acids are not desired because of their corrosive nature [9]. In order to overcome these drawbacks, heterogeneous catalytic systems have been proposed [10-13]. The conversion of cellulose into glucose and the simultaneous hydrogenation of glucose into sugar alcohols, such as sorbitol and mannitol on Ru/C [10], polymer stabilized Ru nanoclusters [11], and Pt and Ru supported by HUSY and γ-Al₂O₃ [12] has been reported. In order to replace the mineral acids in the acid hydrolysis of cellulose, solid acid catalysts such as sulfonated activated carbon (AC-SO₃H) [13], sulfonic acid-mesoporous materials [14], and Brønsted acidic zeolites [12, 13] were used. Higher glucose yields were reported for sulfate modified catalysts than for acidic zeolites. Besides in the hydrolysis of sucrose and starch, sulfonated mesoporous silicas showed higher activities than ion exchange resins and HZSM-5 catalysts [15]. In this sense, sulfated zirconia is expected to show high glucose yields, albeit a significant amount of by-products has been noted [13].

The textural properties of conventional sulfated zirconia are not beneficial with typically relatively low surfaces areas (100-120 m²/g). Much effort has been spent in order to prepare a high surface area sulfated zirconia. Mesoporous silicas have attracted wide-spread interest due to the high surface area (up to 1000 m²/g), large pore volume, and a hexagonal array of uniform pores. The silanol groups on the surface of these materials are neutral or slightly acidic. Combining these beneficial textural properties of ordered mesoporous silicas with the intrinsic acidity of sulfated zirconia by dispersing the latter in the former would greatly enhance the catalytic activity. SBA-n mesoporous materials [16, 17] have higher stability than other typical mesoporous silicas such as of the M41S family [18] due to their thicker walls, which should be beneficial when the aim is to introduce other components into the framework. The introduction of the
zirconia precursor simultaneously with the silicon precursor in the preparation of SBA-15 was shown to be effective for a good distribution of zirconium within the silica framework [19].

In our previous work, we have found indications for strong Brønsted acidity of sulfate modified ZrO$_2$/SBA-15 by $^1$H MAS NMR [20]. The origin of the strong surface acidity in sulfated zirconia has not been unequivocally resolved [21, 22]. Several postulates on the acidity, whether it is related to the sulfate group and various binding structures of this group to the zirconia surface, have been proposed [23-29]. Here, we investigated the surface acidity of a range of ZrO$_2$/SBA-15 composites by infrared spectroscopy of adsorbed carbon monoxide. In addition, temperature-programmed decomposition of adsorbed alkylamines was used to probe the density of surface acidic sites. It is known that, alkyl ammonium ions form upon protonation of amines by Brønsted sites and decompose into the corresponding alkene and NH$_3$ in a narrow temperature range through a reaction similar to the Hoffman elimination [30]. The hydrolysis reactivity of a range of ZrO$_2$/SBA-15 composites was determined using cellobiose as a model substrate. It is a dimer of glucose with β-1,4-glycosidic bonds, providing a useful model compound for the hydrolysis of cellulose.

**Experimental**

**Synthesis of materials**

SBA-15 silica materials were prepared by a well-established procedure [16, 17]. Siliceous SBA-15 was prepared by adding 9 ml of tetraethyl orthosilicate (TEOS) to 150 ml of 1.5 M HCl solution containing 4 g of Pluronic-123 (Aldrich). The mixture was stirred for 24 h at 40 °C and allowed to further react at 100 °C overnight in Teflon bottles. Subsequently, the solid material was obtained by filtration, dried at room
temperature overnight and calcined at 500 °C in an air flow for 5 h. Zirconium was introduced in the synthesis solution simultaneously with TEOS in the form of zirconiumoxychloride (ZrOCl₂·8H₂O, 99.9%, Strem Chemicals). Appropriate amounts of the zirconium precursor were added to obtain final products with 5-25:100 ZrO₂:SiO₂ ratios. The materials are denoted as Zr(x)SBA-15 with x being the ZrO₂ molar amounts per 100 moles SiO₂. Sulfated catalysts were prepared by sulfation in a 0.25 M H₂SO₄ solution for 15 min followed by drying overnight at 80 °C. Al-SBA-15 was prepared by prehydrolysing aluminum iso-propoxide (Acros Organics, 98%) in 10 ml of HCl solution. This solution was then added to the synthesis gel of SBA-15 to obtain Al-SBA-15. The Si/Al ratio is 34 in the final catalyst with a surface area of 903 m²/g. Conventional sulfated zirconia was prepared by calcination of the sulfated zirconium hydroxide provided by MEL Chemicals (XZO 1249/01) at 500 °C for 5 h.

**Characterization**

Elemental analyses were carried out by ICP-OES (Spectro CirosCCD ICP optical emission spectrometer with axial plasma viewing). To extract the metals, the catalysts were dissolved in a 1.5 ml solution of HF/HNO₃/H₂O (1:1:1) acid mixture. The elemental compositions of the catalysts were determined under the reaction conditions as well. In a typical test 10 mg catalyst was added to 5 ml of water at 160 °C for 0-60 min. The catalyst was recovered by centrifugal separation under vacuum and the elemental analysis was performed by using Perkin-Elmer Series II 2400 CHNS analyzer.

TEM images were taken on a FEI T20 electron microscope operating at 200 V. The specimens were dispersed in ethanol and placed on holey copper grids.
The surface areas were measured using nitrogen adsorption isotherms at −196 °C on a Micromeritics ASAP 2000 gas sorption and porosimetry system. The samples were prepared for measurement by degassing at 150 °C for 24 h. Surface areas were calculated by the BET (Brunauer-Emmett-Teller) method and the pore size distributions were determined by using the BJH (Barrett-Joyner-Halenda) method.

FT-IR spectra of the samples were recorded in the range of 4000-400 cm⁻¹ by a Bruker IFS 113v instrument. The spectra were acquired at a 2 cm⁻¹ resolution and averaged over 20 scans. The samples were prepared as thin self-supporting wafers of 5-10 mg/cm² and placed inside a controlled environment infrared transmission cell, capable of heating and cooling, gas dosing and evacuation. Prior to CO adsorption, the catalyst wafer was heated to 450 °C at a rate of 10 °C/min in an oxygen atmosphere. Subsequently, the cell was out-gassed at the final temperature until the residual pressure was below 5x10⁻⁵ mbar. The sample was then cooled to -190 °C. CO was introduced into the cell via a sample loop (0.4 µmol per dose) connected to a Valco six-port valve.

Temperature programmed decomposition (TPD) of i-propylamine (IPAm) was performed in a packed-bed quartz reactor. The effluent gases were analyzed by a Balzers quadrupole mass spectrometer. 100 mg of catalyst was heated at a rate of 5 °C/min to 450 °C in a He flow of 100 ml/min. The sample was then cooled to 100 °C and exposed to excess gaseous IPAm (99.5%, Aldrich) for 10 min. Physisorbed IPAm was removed at 100 °C by purging in 100 ml/min He for 24 h. TPD of IPAm was carried out by heating the sample to 550 °C at a rate of 5 °C/min in 200 ml/min He. The formation of propene (m/e = 41) and ammonia (m/e = 17), i.e. the decomposition products of IPAm, as well as the amount of desorbed IPAm (m/e = 44, 41, and 17) were followed and compared to well-calibrated standards.
Catalytic activity

Cellulbiose hydrolysis was carried out in a lab-scale batch reactor (Autoclave Engineers, 100 ml). Typically, the reactor was charged with a solution of 0.5 wt. % cellulbiose in water to which a predetermined amount of catalyst (0.1 wt. % compared to solvent) was added. Kinetic experiments were performed at 160 °C under a nitrogen pressure of 20 bars. 20 bars nitrogen overpressure was necessary to ensure that the reactants and the products remained in the liquid phase. The start of the reaction was taken as the moment when the reactor contents reached the desired reaction temperature. Although the reactors were heated as fast as possible, the heating duration was 10-12 min. when some reaction already took place. This method is still preferred over injection of the solution after heating, because in the latter method, higher pressures than 20 bars is needed to inject the solution which cannot be achieved with the current set-up. When the initial loss of cellulbiose was traced, it was found that the loss was not more than 10% that is significantly lower than the initial rates. Samples were withdrawn every 30 min for 2 h. Analysis was performed offline using a Waters HPLC system equipped with a H⁺-column (Polymer Lab.) and RI detector. The column temperature was kept constant at 60 °C. The mobile phase was 10 mM sulfuric acid solution which was fed at a flow rate of 0.6 ml/min.

Results and Discussions

Physicochemical properties

The intended compositions, Zr and S contents determined from the elemental analysis, SO₄/Zr ratio and BET surface areas of the catalysts are collected in Figure 1. Pure SBA-15 has a surface area of nearly 800 m²/g, which is consistent with the highly ordered mesostructure seen from TEM image (Figure 1). Upon introduction of zirconia,
the BET surface areas decreased to values between 500 and 600 m$^2$/g, indicating that the introduction of zirconia in SBA-15 has resulted in a less ordered structure than siliceous SBA-15.

**Figure 1.** Electron micrographs of SBA15 (a) and SZrSBA15(b).

The zirconium contents in the calcined materials were lower than the amounts in the synthesis gel, implying that not all Zr was built into SBA-15 and remained dissolved in the synthesis solution. Initially, we used 1 M H$_2$SO$_4$ to sulfate the Zr(x)SBA-15 materials, but this had a strong adverse effect on the textural properties (surface areas below 100 m$^2$/g). A sulfuric acid concentration of 0.25 M was sufficient to provide good sulfation without causing too much loss of surface area. The surface area of the sulfated Zr(x)SBA-15 materials was above 200 m$^2$/g and still much higher than that of conventional sulfated zirconia. The sulfur content of the calcined sulfated samples was about 3.3 wt. % and did not change much with the Zr content. The XRD patterns did not show clear reflections in the low angle region for the zirconium-containing samples, indicating that the long range order of mesopores was absent. No reflections were observed in the high-angle region, implying that either the zirconium atoms were well dispersed or that the zirconia crystals were very small.
Table 1. Zirconia and sulfur contents of the catalysts determined by elemental analysis and the BET surface area of the non-sulfated and sulfated Zr-SBA-15.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Zr</th>
<th>Zr (wt. %)</th>
<th>S (wt. %)</th>
<th>SO₄/Zr molar ratio</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>na²</td>
<td>na</td>
<td>Na</td>
<td>na</td>
<td>773</td>
<td>1.18</td>
</tr>
<tr>
<td>Zr(15)SBA-15</td>
<td>7</td>
<td>5.3</td>
<td>Na</td>
<td>na</td>
<td>586</td>
<td>1.46</td>
</tr>
<tr>
<td>Zr(25)SBA-15</td>
<td>4</td>
<td>10.9</td>
<td>Na</td>
<td>na</td>
<td>506</td>
<td>1.15</td>
</tr>
<tr>
<td>SZr(5)SBA-15</td>
<td>20</td>
<td>4.3</td>
<td>3.5</td>
<td>2.3</td>
<td>313</td>
<td>0.43</td>
</tr>
<tr>
<td>SZr(10)SBA-15</td>
<td>10</td>
<td>10.9</td>
<td>3.4</td>
<td>2.6</td>
<td>311</td>
<td>0.43</td>
</tr>
<tr>
<td>SZr(15)SBA-15</td>
<td>7</td>
<td>5.2</td>
<td>3.4</td>
<td>1.9</td>
<td>284</td>
<td>0.40</td>
</tr>
<tr>
<td>SZr(20)SBA-15</td>
<td>5</td>
<td>8.9</td>
<td>3.2</td>
<td>1.1</td>
<td>261</td>
<td>0.39</td>
</tr>
<tr>
<td>SZr(25)SBA-15</td>
<td>4</td>
<td>10.8</td>
<td>3.3</td>
<td>0.9</td>
<td>246</td>
<td>0.34</td>
</tr>
<tr>
<td>SZr(30)SBA-15</td>
<td>3</td>
<td>13.4</td>
<td>3.1</td>
<td>0.7</td>
<td>203</td>
<td>0.24</td>
</tr>
<tr>
<td>SZ-Commercial</td>
<td>na²</td>
<td>na</td>
<td>7.0²</td>
<td>0.22</td>
<td>123</td>
<td>0.10</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>na²</td>
<td>na</td>
<td>Na</td>
<td>na</td>
<td>903</td>
<td>1.11</td>
</tr>
</tbody>
</table>

¹ not applicable; ² before calcinations

The elemental analysis of the catalysts after hydrothermal treatment at 160 °C (Table 2) indicated that the sulfur is eluted under reaction conditions in both conventional sulfated zirconia and SZr(x)SBA-15 catalysts.
Table 2. Sulfur contents of the catalysts after treatment in water at 160 °C determined by elemental analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>0 min</th>
<th>10 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZr(15)SBA-15</td>
<td>3.40</td>
<td>0.30</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>SZr(25)SBA-15</td>
<td>3.30</td>
<td>0.30</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>SZ-Commercial</td>
<td>7.01</td>
<td>1.03</td>
<td>0.97</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Infrared spectroscopy of adsorbed carbon monoxide

FT-IR spectra in the CO stretching region of SBA-15 after carbon monoxide adsorption at liquid nitrogen temperature is shown in Figure 2a. The spectra exhibit two distinct bands at 2138 and 2158 cm\(^{-1}\). The latter is attributed to CO adsorbed on weakly acidic silanol groups. The band at 2138 cm\(^{-1}\) is due to a weakly perturbed condensed carbon monoxide phase on the surface of SBA-15 [31, 32]. The weak feature at 2110 cm\(^{-1}\) derives from carbon monoxide coordinating with its oxygen atom to the silanol group. The FT-IR spectra in the CO stretching region of Zr(15)SBA-15 catalyst are given in Figure 2b. In the presence of zirconia, an additional band at 2186 cm\(^{-1}\) was also observed. This band was assigned to Lewis acid centers formed by coordinatively unsaturated Zr\(^{4+}\) centers [30]. Increasing CO coverage saturated these sites earlier than the silanol groups, implying that the former sites bind CO stronger than the latter in accordance with the larger shift of the carbon monoxide stretching frequency.

Infrared spectra of CO adsorption on SZr(15)SBA-15 are shown in Figure 2c. Similar to the non-sulfated catalyst, a band at 2138 cm\(^{-1}\) was observed due to the weakly physisorbed CO. The band around 2160 cm\(^{-1}\) was attributed to silanol groups. It was located at a slightly higher wavenumber than that in SBA-15 and Zr(15)SBA-15.
The band at 2186 cm$^{-1}$ due to CO coordinating to low coordinated Zr$^{4+}$ centers disappeared on sulfated samples. This was attributed to complete coverage of the Lewis acid centers by sulfate groups.

**Figure 2.** FT-IR spectra of adsorbed carbon monoxide at liquid nitrogen temperature for (a) SBA-15, (b) Zr(15)SBA-15 and (c) SZr(15)SBA-15.

The infrared spectra of CO adsorption on conventional sulfated zirconia are shown in Figure 3. The band at 2170 cm$^{-1}$ was attributed to the terminal hydroxyl groups on the zirconia surface. The high frequency band was blue-shifting with increasing CO coverage in the region between 2195-2205 cm$^{-1}$. This band was assigned to the C-O stretching mode of carbon monoxide interacting with Lewis acid centers, *i.e.* the Zr$^{4+}$ centers, of varying acidity.
The infrared spectra in the silanol stretching region of SBA-15, Zr(15)SBA-15 and SZr(15)SBA-15 catalysts are shown in Figure 4a-c, respectively. The spectrum of SBA-15 exhibits a sharp feature at 3747 cm$^{-1}$ which is ascribed to the isolated, non-hydrogen bonded silanol groups on the surface. The broad tail extending towards 3400 cm$^{-1}$ is due to the hydrogen bonded silanol groups. CO adsorption on isolated silanol groups weakens the hydroxyl bond and leads to a perturbed band around 3653 cm$^{-1}$ with a frequency shift of 94 cm$^{-1}$. The silanol stretching region of the Zr(15)SBA-15 catalyst is similar to pure SBA-15. The isolated silanol groups are identified by the band at 3747 cm$^{-1}$. The tail is preserved and its extension to 3400 cm$^{-1}$ indicates the presence of hydrogen bonded a silanol groups. The shift of the hydroxyl groups upon CO adsorption is very similar to SBA-15. This indicates the silanol groups are still only weakly acidic in the zirconia-substituted SBA-15. The corresponding hydroxyl region for SZr(15)SBA-15 is shown in Figure 4c. At low CO coverage, the hydroxyl band is
perturbed to a wavenumber of 3601 cm\(^{-1}\) from 3745 cm\(^{-1}\), corresponding to a shift of 144 cm\(^{-1}\) upon CO adsorption. With increasing CO coverage, the band of perturbed OH broadens and \(\Delta \nu_{\text{OH}}\) at high CO coverage is 106 cm\(^{-1}\).

**Figure 4.** FT-IR spectra of adsorbed carbon monoxide at liquid nitrogen temperature in the hydroxyl stretching region for (a) SBA-15, (b) Zr(15)SBA-15 and (c) SZr(15)SBA-15.

This can be explained by the presence of stronger acidic sites giving rise to \(\Delta \nu_{\text{OH}} = 144\) cm\(^{-1}\) in close proximity to weakly acidic sites (\(\Delta \nu_{\text{OH}} = 94\) cm\(^{-1}\)). An IR frequency shift of 144 cm\(^{-1}\) upon CO adsorption on SZr(15)SBA-15 is very close to the 139 cm\(^{-1}\) shift reported earlier for a conventional sulfated zirconia catalyst [33].

Previous FT-IR investigations provide evidence that sulfation of zirconia enhances the strength of the bridging zirconia hydroxyl groups, that is Zr-(OH)-Zr, and eliminates the terminal ones (i.e., ZrOH) [25]. In addition, it creates a new type of Brønsted acid site, presumably protons forming multicentered or single bonds with...
sulfate ions. These protons are hydrogen bonded to the surface [26]. Similarly, when zirconia included SBA-15 catalyst was modified by sulfation, the Lewis acid centers were covered by sulfate groups and the terminal hydroxyls of zirconia were eliminated. As a result strong Brønsted acidity is developed.

The presence of strong Brønsted acidity was indicated by the sulfate and the silanol stretching regions. The larger perturbation in the silanol region for the sulfated catalyst than the non-sulfated catalysts can be described as follows. Either the acidic proton bonded to the sulfate group was directly probed or the oxygen of the silanol group is involved in hydrogen bonding with the adjacent acidic proton bonded to the bisulfate group shown in Figure 5. The red shift observed in hydroxyl region for SZr-SBA-15 catalysts is not much higher than that for conventional sulfated zirconia. Therefore, we conclude that our catalysts have a slightly higher acidic strength than conventional sulfated zirconia. The $\Delta \nu_{OH}$ of 144 cm$^{-1}$ is higher than the shift for weakly acidic silanol, yet lower than that of strongly acidic zeolites (stabilized faujasite zeolite, $\Delta \nu_{OH} \approx 300$ cm$^{-1}$) [34]. The IR spectra of the S=O stretching region for SZr(15)SBA-15 are presented in Figure 6. CO adsorption brings about a positive frequency shift of about 26 cm$^{-1}$. This shift indicates an increase of the S=O bond strength and is attributed to the interaction of CO with the strongly acidic proton, as weakening of the SO–H bond upon interaction of the proton with CO causes an increase of the S=OH bond strength. This observation provides an indirect indication for the presence of protonic sites connected to the sulfate groups. Indeed, direct observation of the strong Brønsted acid protons in sulfated zirconia catalysts is not straightforward, likely because of the strong hydrogen bonding to adjacent surface groups [20].
Figure 5. Proposed binding structure of sulfate to zirconia centers in SBA-15 and the hydrogen bonding between the acidic proton of the sulfate group and the surface oxygens.

Figure 6. FT-IR spectra of adsorbed carbon monoxide at liquid nitrogen temperature in the region of S=O stretch for SZr(15)SBA-15.

Temperature-programmed decomposition of IPAm

The evolution of propene during temperature programmed IPAm decomposition for the various catalysts is shown in Figure 7. No IPAm decomposition is observed for siliceous SBA-15. For the zirconia-containing catalysts, decomposition of adsorbed IPAm takes place between 310 and 360 °C with a maximum around 340 °C. In contrast,
the decomposition in the sulfated catalysts occurred in the interval 290-340 °C with a maximum around 312 °C. In Table 3, the amount of decomposed IPAm as well as the decomposition temperature are given for these catalysts. Introduction of zirconia in the silica results in the creation of sites capable of chemisorbing and decomposing IPAm.

**Figure 7.** Production of propene from i-propylamine decomposition during TPD for the various catalysts. Actual Zr loadings for zirconium-containing silicas are indicated left.

Upon sulfation, the decomposition temperature for Zr(15)SBA-15 decreases considerably. The difference should be due to stronger activation of the chemisorbed IPAm complex. Table 3 also gives the results for two reference samples HZSM-5 and Al-SBA-15. The former contains exclusively aluminum in the zeolite framework and the amount of IPAm decomposed corresponds to the aluminum density. The latter contains mainly Lewis acidic Al sites on the surface of SBA-15. IPAm chemisorbed to
these Lewis acidic sites decomposes at a higher temperature and the result is very similar to that of the non-sulfated Zr(x)/SBA-15 samples.

**Table 3.** IPAm decomposition temperatures amounts for different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Zr loading (wt. %)</th>
<th>(N_{\text{IPAm, total}}) (mmol/g cat.)</th>
<th>(T_{\text{max,1}}) (°C)</th>
<th>(N_{\text{IPAm,1}}) (mmol/g cat.)</th>
<th>(T_{\text{max,2}}) (°C)</th>
<th>(N_{\text{IPAm,2}}) (mmol/g cat.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr(15)SBA-15</td>
<td>5.3</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
<td>340</td>
<td>0.09</td>
</tr>
<tr>
<td>SZr(5)SBA-15</td>
<td>4.3</td>
<td>0.26</td>
<td>314</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SZr(10)SBA-15</td>
<td>3.7</td>
<td>0.14</td>
<td>313</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SZr(15)SBA-15</td>
<td>5.2</td>
<td>0.50</td>
<td>313</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SZr(20)SBA-15</td>
<td>8.9</td>
<td>0.37</td>
<td>307</td>
<td>0.36</td>
<td>342</td>
<td>0.01</td>
</tr>
<tr>
<td>SZr(25)SBA-15</td>
<td>10.8</td>
<td>0.39</td>
<td>308</td>
<td>0.36</td>
<td>341</td>
<td>0.03</td>
</tr>
<tr>
<td>SZr(30)SBA-15</td>
<td>13.4</td>
<td>0.27</td>
<td>308</td>
<td>0.23</td>
<td>342</td>
<td>0.04</td>
</tr>
<tr>
<td>HZSM-5(^1)</td>
<td>-</td>
<td>0.82</td>
<td>310</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al-SBA-15(^2)</td>
<td>-</td>
<td>0.09</td>
<td>345</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) Si/Al = 20; \(^2\) Si/Al = 34.

It is then straightforward to conclude that IPAm in the non-sulfated catalyst adsorbs to Lewis acid Zr\(^{4+}\) centers, whereas this adsorption state should be absent after sulfation. Instead, the Bronsted acidic sites adsorb IPAm more strongly through protonation of the alkylamine, which results in a lower decomposition temperature. For the series of sulfated Zr(x)/SBA-15, the amount of decomposed IPAm first increases up to a value of 0.5 mmol/g for SZr(15)SBA-15 and then decreases with increasing zirconium loading indicating that there is an optimum dispersion of zirconia in the material. The decrease
in zirconia dispersion above a zirconium content of 5.2 wt.% (SZr(15)SBA-15) can be attributed to the partial loss in the long range order of silica.

For SZr(20)SBA-15 and the samples with higher Zr loading, we find that there are two peaks in propene production, one main peak around 310 °C and the other smaller contribution around 340 °C. The contribution of the latter peak increases somewhat with the zirconium loading. As its location is similar to the peak observed for the non-sulfated sample, we infer that these samples contain a small amount of Lewis acidic Zr\(^{4+}\) centers. Indeed, the SO\(_4\)/Zr ratio decreases with increasing Zr loading of the catalysts above Zr contents greater than 3.7 wt.%.

**Catalytic activity**

The conversion of cellobiose and the yield to glucose at a reaction temperature at 160 °C are given in Figure 8. Comparing the SBA-15 based catalysts; the sulfated catalysts are more active in cellobiose conversion. Complete cellobiose conversion is obtained after a reaction time of 120 min for SZr(15)SBA-15 and SZr(25)SBA-15. In comparison, Zr(15)SBA-15 displays a much lower activity. The activity of an Al-SBA-15 reference catalyst is also very low.
Figure 8. Cellobiose conversion (left) and glucose yield (right) as a function of reaction time for a large set of catalysts ($T = 160 \, ^\circ\text{C}$; $p_{N_2} = 30 \, \text{bar}$; autoclave; 0.5 wt% cellobiose and 0.1 wt% catalyst in water).

The lower activities of Zr(15)SBA-15 imply that the hydrolysis of cellobiose is more favorable on Brønsted acid sites than on Lewis acid sites. The activity of the conventional sulfated zirconia material is very close to the sulfated Zr($x$)SBA-15 materials. On the other hand, the glucose yields of the sulfated Zr($x$)SBA-15 are much higher than conventional sulfated zirconia. Catalysts with Brønsted acid sites showed high selectivity for glucose in a previous study [14]. Hence, the higher yields of glucose on sulfated Zr($x$)SBA-15 in comparison to conventional sulfated zirconia is most likely due to the absence of Lewis acid sites, known to catalyze the dehydration of glucose, in the composite catalysts. The sulfur content of the conventional sulfated zirconia catalyst as well as the SZr($x$)SBA-15 catalysts decreases under the reaction conditions. The incorporation of sulfated zirconia into SBA-15 structure does not improve the hydrothermal stability of the catalysts and this remains the limitation for the catalytic application of the sulfated zirconia catalysts.
Conclusions

Strong Brønsted acidity of sulfated zirconia-SBA-15 catalysts were demonstrated by FTIR spectroscopy of surface hydroxyls upon CO adsorption and TPD of IPAm decomposition. The strong acidity of these materials results from the sulfation of zirconia patches included in the SBA-15 silica material. The acidity before sulfation stems from Lewis acidic Zr\(^{4+}\) centers. The intrinsic Brønsted acidity of a sulfated zirconia modified SBA-15 is close to that of conventional sulfated zirconia. Sulfated zirconia dispersed throughout SBA-15 is an efficient catalyst for the scission of the 1,4-\(\beta\) glycosidic bonds in cellobiose which is a model reaction for the critical step in the depolymerization of cellulose into valuable chemicals. The present study suggests that the isolated Brønsted acid sites catalyze cellobiose hydrolysis resulting in high glucose yields. On the other hand, catalysts which contain Lewis acidic sites next to these protons such as conventional sulfated zirconia exhibit a lower glucose yield.

Acknowledgements

One of the authors, V.D., is grateful for the doctoral scholarship and exchange grants from the Scientific and Research Council of Turkey (TUBITAK) through the BDP program. National Science Foundation supported this work through grant CTS-0455965. This work has been partially supported by Dutch Technology Foundation (STW) under a VIDI grant. We thank the MEL Chemicals for providing the sulfated zirconium hydroxide. We would like to acknowledge Jie Fan and Galen Stucky (UC, Santa Barbara) for transmission electron microscopy measurements.

References

APPENDIX 3. STUDY ON THE HYDROTHERMAL STABILITY OF SULFATED ZIRCONIUM MODIFIED SBA-15

A paper to be submitted to Applied Catalysis A: General

Haiyang Zhu¹, Basak Cinlar¹, Shaojun Miao¹, Brent H. Shanks¹

¹Department of Chemical and Biological Engineering, Iowa State University, Ames

Authorship roles:
Zhu: Primary author, designed and conducted the hydrothermal stability experiments.
Cinlar: Second author, conducted part of the hydrothermal stability experiments.
Miao: Third author, conducted kinetic experiments.
Shanks: Principal investigators.

Abstract
Zirconium sulfate, zirconium oxychloride, and zirconium n-propoxide were used as precursors to synthesize sulfated zirconium modified SBA15. Together with the different synthesis parameters, the influence of these precursors on the final zirconium content, textural properties and the hydrothermal stability were investigated by N₂ adsorption-desorption isotherms, inductively coupled plasma optical emission spectrometry (ICP-OES), thermogravity (TG), and X-ray diffraction (XRD). Also their catalytic activity was measured for a model reaction, the esterification of ethanol and acetic acid. The results indicated that (1) calcined SBA15 showed better hydrothermal stability than extracted SBA15 samples, suggesting that surface hydroxyl group had a negative effect in hydrothermal stability; (2) the final zirconium content varied with the precursors due to the
different hydrolysis products such as acid and alcohol; (3) the samples with low zirconium content showed better hydrothermal stability than those with high zirconium content; (4) the samples would lose their active sites with the dissolution of the sulfate ions. The possible mechanisms for these phenomena were proposed in this work.

**Introduction**

Sulfated zirconia has received great interest as catalyst due to its activity in many important reactions including isomerization, cracking, and fatty acid esterification with methanol [1-9], but its utilization is limited by its lower surface area. To increase the surface area, many attempts have been made by using different type of supports that can provide thermal stability as well [6, 10, 11]. The precursor and the synthesis procedure were reported to enhance the stability, but there are only few studies focused on this aspect and a detailed understanding is not provided. Outlining the effect of the precursor and the synthesis procedure on textural properties and relating those to the stability of supported sulfated zirconia is of great importance because it will allow for extended utilization of catalyst in many different reactions.

In order to combine the extraordinary acidic properties of sulfated zirconia with large surface areas, sulfated zirconia have been tried to be supported on different materials [6, 10, 11]. Due to their large surface areas with ordered structure, mesoporous silica materials are one of the potential supports for the dispersion of sulfated zirconia [6, 10, 11]. With the introduction of zirconia into the framework of MCM41, enhanced thermal stability, acidic strength and increased number of acidic sites were reported [12-15]. Similarly, when high loadings of zirconia was introduced into MCM41 particles via evaporation induced self
assembly, improved hydrothermal stability was obtained as compared to pure MCM41 particles that was in fact proportional on the loading density of zirconia [16]. So far, most of the effort was spend on the incorporation of zirconium into the MCM-41 framework. However, with its larger pore size and better thermal stability, SBA15 is a better candidate among the mesoporous silica supports. Such incorporation will enable utilization of the catalyst for reactions with large molecules at relatively high temperatures such as the esterification of the long chain fatty acids [17, 18] which is an important reaction for biorenewable industry. Also if hydrothermal stability is provided, the catalyst will be a potential candidate for polysaccharide hydrolysis reactions, another important reaction for a biomass based economy.

For the incorporation of sulfated zirconia into SBA-15, post synthesis grafting is the common method as the acidic medium during SBA15 synthesis prevents the hydrolysis of zirconium. In the post synthesis grafting, the pH of the medium is readjusted to an alkaline value after the formation of mesoporous structure allowing for zirconium hydrolysis [19-22]. Using this method, SBA15 samples with high zirconium contents were synthesized, which showed high activity in acid catalyzed reactions containing large molecules [19, 20]. However, in this method the uniform pore structure may be destroyed and the channels may be blocked [23]. Chen et al developed a direct synthesis method for sulfated zirconium incorporated SBA15 by using zirconium propoxide and ammonium sulfate as the precursors. The catalysts, synthesized according to this method attained well ordered mesoporous structure and showed better activity for the esterification of long-chain free fatty acids than the conventional sulfated zirconia [22].
Another application area for these catalysts will be the condensed phase aqueous reactions with large molecules that require hydrothermal stability of the catalyst. Due to the extraordinary properties of water as solvent, different stability concerns may arise in aqueous phase as compared to other solvents or gas phase reactions. Investigation of hydrothermal stability is therefore an important element in catalyst characterization, however only limited literature can be found on this aspect. The zirconium precursors and the synthesis procedure are reported to influence the hydrothermal stability, but details were not explained.

In this paper, the effect of synthesis method and different zirconium precursors, i.e zirconium sulfate, zirconium oxychloride, and zirconium n-propoxide, on the textural and catalytic properties, the final zirconium content and on the hydrothermal stability of the final material was investigated using N\textsubscript{2} adsorption-desorption isotherms, inductively coupled plasma optical emission spectrometry (ICP-OES), thermogravimetry (TG), X-ray diffraction (XRD) and the model reaction, esterification of ethanol and acetic acid. The possible reason for the poor hydrothermal stability of zirconium modified SBA15 was proposed.

**Experimental**

**Synthesis of sulfate Zr-SBA15 materials**

For the synthesis of zirconium substituted SBA-15 samples (Zr-SBA15), the micelle template was prepared using Pluronic 123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) as surfactant and tetraethylorthosilicate (TEOS) was used as silicon source. Zirconium sulfate, zirconium oxychloride and zirconium n-propoxide were the zirconium precursors used in this study.
Synthesis of sulfated Zr-SBA15 using zirconium sulfate as a precursor

4 g of surfactant was dissolved in 120 ml deionized water. 20 ml of 37 wt% HCl was mixed with the resultant solution. The requisite amount of zirconium sulfate and 9.2 ml of TEOS were added to the mixed solution. After vigorous stirring at 40°C for 24 h and aging at 100°C for 24 h, the sample was collected by filtration and calcined at 550°C for 4 h at a ramp of 1°C/min. These samples were denoted as xxZrS, for example, 15ZrS represented the sample by using zirconium sulfate as precursor and the zirconium molar loading is 15% (Si/Zr molar ratio of 17:3).

Synthesis of sulfated Zr-SBA15 using zirconium oxychloride as a precursor

The same procedure was followed except that requisite amounts of zirconium oxychloride were added instead of zirconium sulfate. The samples were sulfated before and after calcination by immersing in 1 mol/L sulfuric acid solution for 2 h. These samples were denoted as xxZrO, for example, 15ZrO represented the sample by using zirconium oxychloride as precursor and the zirconium molar loading is 15%.

Synthesis of sulfated Zr-SBA15 with zirconium n-propoxide as a precursor

The sulfated Zr-SBA15 with zirconium n-propoxide as a precursor was synthesized according to the suggested method by Chen et al [22]. Again a similar procedure to that of sulfated Zr-SBA15 with zirconium sulfate was followed, but this time the requisite amounts of zirconium n-propoxide and ammonium sulfate (the SO₄²⁻/Zr molar ratio of 1.0) were added together with 9.2 ml of TEOS. These samples were denoted as xxZrP, P representing the zirconium n-propoxide precursor and xx representing the zirconium molar loading.
Characterization

Nitrogen adsorption isotherms were obtained at 196°C on a Micromeritics ASAP 2020. The surface area and the pore volume/pore size distribution were calculated by using BET and BJH methods, respectively. Zirconium, silicon and sulfur contents were determined by elemental analysis via ICP-OES, where the samples were prepared by dissolving ca. 0.05g in 4 ml HF/HNO₃/H₂O (1:1:1) acid solution. X-ray diffraction (XRD) was carried out on Siemens D500 X-ray diffractometer with a Cu Kα radiation source. The X-ray tube was operated on 45 kV and 30 mA. For the hydrothermal stability testing, about 0.2 g of catalyst was dissolved in 50 ml water, and was treated to 145°C for 2 h in 75 ml steel reactor under nitrogen pressure to maintain condensed phase. The recovered catalysts were tested for their textural properties and zirconium and sulfur contents.

The esterification of acetic acid with methanol was carried out in a two-necked 100 ml flask with a reflux condenser, which was placed in a thermostatic bath with a magnetic stirrer. In a typical experiment before the reaction, reagent mixtures (acetic acid 3 M, methanol 6 M, as well as the solvent 1,4-dioxane to balance the total volume to 50 ml) were heated to the desired reaction temperature while being vigorously stirred. Once the desired temperature was reached, the reaction was started by introducing the catalyst. Here, acetic acid was selected as the representative of organic acid amount present in bio-oil generally. A microscale syringe was used for sampling at defined time intervals including the time just prior to catalyst charging as the zero point. A Varian GC3800 gas chromatograph equipped with a CP-select 624CB column (0.53 mm × 75m × 3 μm) and a FID detector was used for sample analysis. The concentrations of all species except water were accurately quantified. The overall mass balance was more than 98%.
Results and Discussion

After the formation of the silica template, the surfactant from the structure can be removed either via calcination or via solvent extraction. The effect of these two methods on textural properties is demonstrated in Figure 1, where the pore size distributions are plotted for SBA15 before and after the hydrothermal treatment for both calcined and extracted samples. As indicated by sharp peaks, SBA15 has a very narrow pore size distribution for both of the calcined and extracted samples before the hydrothermal treatment. N\textsubscript{2} adsorption and desorption isotherms (not presented in this paper), indicated a similar pore structure for calcined and extracted SBA15. After the hydrothermal treatment, the extracted samples lost their ordered mesoporous structure; while the calcined samples kept their structure well with the pore size increasing from 8.4 to 9.6 nm. These results indicated that the calcined samples had a better hydrothermal stability than the extracted samples.

Figure 1. Pore size distribution results for calcined and extracted SBA15 before and after hydrothermal treatment.
A possible reason for better hydrothermal stability of the calcined samples can be the absence of hydroxyl groups. The samples lost most of the surface hydroxyl groups when calcined at 550°C [24, 25]. Such a loss did not occur during the extraction which was confirmed by TG results as shown in Figure 2. The weight loss for SBA15 in the range of 50–200°C was attributed to the physically adsorbed water. Whether calcined or extracted, the weight loss for SBA15 is ~2-3 wt% in this range. In addition, the extracted SBA15 lost 8.2 wt% in 250–500°C, that can be attributed to the removal of the residual surfactant in the pores and the condensation of surface hydroxyl group [24]. The absence of the weight loss at temperature interval 250-500°C for the extracted sample indicates that most of the hydroxyl groups were removed during calcination. Similar weight loss trend was also observed for MCM41 [26]. The hydroxyl groups are more prone to interact with water inducing hydrolysis of silica structure. As a result, the larger amount of surface hydroxyl groups in the extracted sample decrease its hydrothermal stability. Therefore the samples in this study were prepared via calcination for better hydrothermal stability.

![Figure 2. TGA results for calcined and extracted SBA15 sample.](image-url)
To validate the synthesis methods with different precursors for the dispersion of zirconia, XRD results for Zr-SBA15 samples with high zirconium loadings are shown in Figure 3. XRD results for crystalline zirconia in the mixture phase of tetragonal and monoclinic is also included for comparison. None of the diffraction peaks of crystalline zirconia could be observed for any of the zirconium incorporated SBA15 prepared with different precursors indicating that zirconium was introduced into the SBA15 skeletal [22, 27].

![Figure 3. XRD results for Zr-SBA15 samples with different precursors at high zirconium loading.](image)

Although high zirconium dispersions were achieved for all the precursors, the zirconium contents are generally lower than what was anticipated due the highly acidic conditions for SBA15 synthesis. The highly acidic synthesis conditions for SBA15 hinder the hydrolysis and condensation of zirconium into the structure resulting in lower zirconium contents than anticipated. ICP-OES was used to measure the Si/Zr molar ratio for the resulting materials.
For all precursors, most zirconium ions could not incorporate into the skeletal of SBA15 and were washed off during filtration, as presented in Table 1. Moreover, the zirconium content in the resulting Zr-SBA15 sample was greatly influenced by the precursors. The zirconium contents in those samples by using zirconium sulfate as precursor were much less than those samples by using zirconium oxychloride and zirconium n-propoxide. This can be explained by the different hydrolysis products of the precursors as shown by the equations 1-3 for the related reactions below.

\[ \text{Zr(SO}_4\text{)}_2 + 4\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4 + 2\text{H}_2\text{SO}_4 \quad \text{(Equation 1)} \]
\[ \text{ZrOCl}_2 + 3\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4 + 2\text{HCl} \quad \text{(Equation 2)} \]
\[ \text{Zr(n-C}_3\text{H}_7\text{O)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4 + 4\text{n-C}_3\text{H}_7\text{OH} \quad \text{(Equation 3)} \]

For the hydrolysis of 1 mole of zirconium ion, 4, 2 and 0 moles of proton ions are produced for zirconium sulfate, zirconium oxychloride and zirconium n-propoxide, respectively, as shown in these equations. As a result of the acid concentration of the solution was further increased, that inhibited the condensation of zirconium hydroxide in the order of the precursor: zirconium n-propoxide < zirconium oxychloride < zirconium sulfate. Furthermore, it was proposed that the alcohol produced during the hydrolysis of zirconium n-propoxide decreased the proton concentration around surfactant, which led to faster condensation of zirconium hydroxide and thereby higher zirconium contents [28, 29].

In this study, the influence of alcohol on the zirconium content of the final material was further investigated by modifying the synthesis medium with alcohol addition. When methanol or isopropanol was added to the initial solution with an alcohol/Zr molar ratio of 4, the final Si/Zr ratio decreased from 88.8 to 45.3 and 60.6 for the samples prepared with
zirconium sulfate in the case of methanol and isopropanol, respectively. Similar improvement was observed with the addition of methanol when zirconium oxychloride was used as precursor also. These results suggested the existence of alcohol in the solution might promote the incorporation of zirconium ions into SBA15 structure. As reported by Chen et al. [28] and Denkova et al. [29], alcohol affects the morphologies of triblock copolymer micelles in the solution by the interacting with the copolymer. The increased alcohol concentration around the surfactant micelles leads to a decreased the proton and water concentration around them. Although the hydrolysis rate of zirconium decreases with the decreasing proton concentration, the condensation rate of zirconium hydroxide increases [30, 31] resulting in greater incorporation of zirconium into the SBA15 structure. As a result, the zirconium content in the structure was higher when extra alcohol was added to the solution.

For the sulfonation, the Zr-SBA15 samples were immersed in 0.25 M, 1.0 M sulfuric acid or 1.0 M ammonium sulfate solutions. Due to the coordination between sulfate and zirconium ions, sulfate ions are absorbed by Zr-SBA15 creating Bronsted acid sites [22]. Both ICP and acidity titration results indicated that sulfate ions cannot be absorbed on pure SBA15 without zirconium loadings following the same procedure. It is suggested that the zirconium ions play an important role in the absorption of sulfate ions. However, during the sulfonation zirconium ions may leach from Zr-SBA15 and the mesoporous structure may be destroyed because of the acidity of sulfuric acid and ammonium sulfate solution. After immersed into 0.25 and 1.0 M of sulfuric acid solution, the Si/Zr ratio in the final materials increased from 34.5 to 41.7 and 88.1, respectively. For the samples immersed in ammonium sulfate solution, the Si/Zr molar ratio increased from 34.5 to 55.6. Among the tested
samples, the sulfonation with 1.0 M sulfuric acid resulted in the highest acidity density and lowest zirconium content in the final samples.

Among the Zr-SBA15 samples with different precursors, ZrS samples had the lowest zirconium content; indeed that final zirconium content did not alter much according to the initial loading of zirconia. However, the hydrothermal stability of ZrS samples was influenced by the initial zirconium loading. Figure 4 showed the pore size distribution results of ZrS samples before and after hydrothermal treatment. Before hydrothermal treatment, all samples have a narrow pore size distribution at ~10.7 nm. After hydrothermal treatment, only the sample with low zirconium loading (5%) maintained its mesoporous structure, and 15% and 25% ZrS materials lost their ordered structure. For the 5% ZrS, the pore size increased from 10.7 to 12.1 nm with hydrothermal treatment similar to what was observed with calcined SBA15 sample.

![Figure 4. Pore size distribution results for ZrS samples with different zirconium loadings before and after hydrothermal treatment.](image)
Figure 5 shows the pore size distribution results of ZrO samples as synthesized, after sulfonation and after hydrothermally treated. For the ZrO samples the introduction of zirconium at high concentration (25%) led to a wide pore size distribution, but the 5% and 15% loaded ZrO samples showed narrow pore size distributions as synthesized. After the sulfonation, the 15% loaded ZrO also lost its ordered structure. Only the 5% ZrO sample kept its structure, but again a slight increase in the average pore size was observed from 10.5 to 11.0 nm.

**Figure 5.** Pore size distribution results for ZrO samples with different zirconium loadings before and after sulfated and after hydrothermally treated.
ZrP samples had higher zirconium content as compared to the samples prepared by other two precursors. At all loadings, the ZrP materials maintained a well ordered mesoporous structure with a narrow pore size distribution, even at high zirconium loading, that is different from the samples prepared by other two precursors. However, all of the ZrP samples lost their structure during hydrothermal treatment, as shown in Figure 6.

**Figure 6.** Pore size distribution results for ZrP samples with different zirconium loadings before and after hydrothermal treatment.

Based on the pore size distribution results above, it can be concluded that the samples with low zirconium content have better hydrothermal stability than those with high zirconium content. After the hydrothermal treatment, only the sample with low zirconium content maintained its structure and kept its narrow pore size distribution with a slight
increase in the pore size. The same trend was also observed in the hydrothermal treatment of calcined SBA15 sample.

The increase in the pore size during the hydrothermal treatment can possibly be explained with the following mechanism. As mentioned above, the presence of surface hydroxyl groups had a negative effect on the hydrothermal stability of SBA15 structure by interacting with water molecules and initiating the hydrolysis of silica on the surface layer. During the hydrothermal treatment, the hydrolysis of silica on the surface occurs much faster due to elevated temperatures and finally the hydrolysis product departs from the pore. This way the silicon atoms are peeled from the surface layer by layer leading to an increase in the pore size. Also the high vapor pressure of water at this high temperature has a role in destroying pore structure.

A similar process can be speculated for the zirconium doped SBA15 materials also, where the zirconium ions are hydrolyzed and form zirconium hydroxide that dissolves into solution. In fact, zirconium ions are more prone for hydrolysis as compared to silica. Extraction of zirconium ions to acidic solution was observed even at temperature during synthesis. Furthermore, hydrolysis of zirconium continued to occur during the aging process, but the presence of surfactant helped to maintain the regular structure. After the surfactant was removed by calcination, the mesoporous structure with defects was maintained which are more prone to start a structural breakdown. The density of the defects in the final product is most probably proportional to the initial zirconium loading. The samples with large amount of defects were less stable than those with small amount of defects in hydrothermal treatment, and the hydrothermal stability was independent of the final zirconium content. This can be used to explain the different hydrothermal stability of
ZrS samples with similar final zirconium contents. The lower the initial zirconium loading was, the lower was the defect density in the final material and the more hydrothermally stable it was.

Although this type of defects for zirconium modified SBA15 was not reported elsewhere, a similar phenomenon was documented for ZSM5, mordenites, and other type of zeolites on which the defects were created during the dealumination [32-34]. When treated in hot steam, aluminum ions are washed off from the structure of zeolites and the defects with four silanols are created [34]. These defects play an important role in the incorporation of other atoms into the dealuminated zeolite structure [33]. Alternatively, the dealumination process can be carried out at room temperature in the presence of hydrochloric acid at high concentrations. Accordingly it can be suggested that the existence of acidic sites on SBA15 accelerates leaching of zirconium.

The amount of zirconium in the final structure affected the sulfate ion density of the final material directly. The Si/S ratio followed the same trend as the Si/Zr ratio, both of which are presented in Table 1 for the as prepared and hydrothermally treated samples. For example, only trace of sulfur could be found in ZrS samples due to the low zirconium content. Also for ZrO samples, the S/Si molar ratio increased from ~40 to ~200 after hydrothermal treatment indicating most sulfate ions were removed with the loss of zirconium. The titration results showed that the total acid capacity of 25ZrO samples decreased from 0.83 to 0.01 mmol/g with the hydrothermal treatment that agrees with ICP results.
Table 1. Zirconium and sulfur contents in the resulting samples measured by ICP.

<table>
<thead>
<tr>
<th></th>
<th>ZrS</th>
<th></th>
<th></th>
<th>ZrO</th>
<th></th>
<th></th>
<th>ZrP</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 %</td>
<td>15 %</td>
<td>25 %</td>
<td>5 %</td>
<td>15 %</td>
<td>25 %</td>
<td>5 %</td>
<td>15 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Initial Si/Zr</td>
<td>19</td>
<td>5.67</td>
<td>3</td>
<td>19</td>
<td>5.67</td>
<td>3</td>
<td>19</td>
<td>5.67</td>
<td>3</td>
</tr>
<tr>
<td>Si/Zr by ICP</td>
<td>97.8</td>
<td>88.8</td>
<td>95.8</td>
<td>35.6</td>
<td>34.5</td>
<td>19.2</td>
<td>80.0</td>
<td>20.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Si/Zr sulfated</td>
<td></td>
<td></td>
<td></td>
<td>137.4</td>
<td>88.1</td>
<td>82.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si/S by ICP</td>
<td>∞</td>
<td>441.6</td>
<td>394.3</td>
<td>42.8</td>
<td>34.8</td>
<td>46.2</td>
<td>∞</td>
<td>36.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Si/S after treated</td>
<td>187.0</td>
<td>155.8</td>
<td>198.4</td>
<td>242.6</td>
<td>194.5</td>
<td>215.7</td>
<td>∞</td>
<td>39.0</td>
<td>16.6</td>
</tr>
</tbody>
</table>

The high sulfur content of the ZrO samples before hydrothermal treatment can be explained by the presence of defects. Removal of zirconium and the formation of defects were already observed for the 15ZrO sample during the introduction of sulfate ions, in fact the material collapsed. However at low Zr loading, the presence of defects might have facilitated the introduction of sulfate ions into the structure, similar to the defects in zeolites used to incorporate other ions [33]. The sulfate ions trapped in these defects were hard to be washed out at room temperature and created the acid sites on the catalyst. However, they were released after the collapse of these defects during the hydrothermal treatment.

For ZrP samples, most of the sulfur stayed in the structure after hydrothermal treatment as most of the zirconium ions according to the ICP results. However, the titration results showed that the acidity density on 15ZrP and 25ZrP samples is 0.07 and 0.04 mmol/g, respectively, indicating not all to sulfur that was introduced into the structure, created acidic
sites in these samples or ammonium ions might have neutralized the acid sites in the of sulfonation with ammonium sulfate. In any case, the poor hydrothermal stability prohibits the use of ZrP catalysts in aqueous phase reactions.

Figure 7 shows the activity of sulfated ZrO, 25ZrP, and hydrothermally treated sulfated 25ZrO samples for the esterification of ethanol and acetic acid. For comparison, the activity of SBA15 functionalized with 10 mol% of sulfonic group is also presented. The ZrO samples showed comparable activity to the SBA15 functionalized with 10 mol% of sulfonic group, but the activity of 25ZrO decreased dramatically after being hydrothermally treated that is in agreement with the titration results.

![Figure 7](image-url)  
Figure 7. Ethanol conversions in esterification of ethanol and acetic acid in the presence of ZrO, 25ZrP, and hydrothermal treated 25ZrO samples.
In addition, the activity of ZrO samples were not related to the zirconium content, but followed the same trend with the sulfur content as determined by ICP. On the other hand, ICP results indicated higher sulfur content for 25ZrP sample than the ZrO samples, but the activity of 25ZrP was much lower than ZrO samples. Therefore it can be concluded that neither the zirconium content nor the sulfur content are the sole indicators of catalytic activity, but the resultant number of acidic sites, measured by acid-base titration, is important for the catalytic activity.

Conclusions

The zirconium content of the final material was influenced greatly by the choice of zirconium precursor because different products formed during hydrolysis of different precursors, such as acid and alcohol, changing the nature of the synthesis medium. The samples prepared by using zirconium propoxide as precursor had the highest zirconium content. As reported elsewhere, the introduction of zirconium ions into SBA15 could enhance the thermal stability of SBA15. However, our results indicated that the introduction of large amount of zirconium leads to poor hydrothermal stability due to the faster hydrolysis of zirconia as compared to silica. In addition, the surface hydroxyl groups have a negative effect in the hydrothermal stability of SBA15.

References