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Catalytic domains in porous catalysts

by

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Abstract

Understanding of the catalytic domains within porous catalysts is essential for control of these systems in order to obtain desired reaction yields and selectivities. This body of work consists of studies on two types of porous catalysts, mesoporous silica and zeolites, that can have interesting cooperative catalytic interactions between the inorganic framework and organic molecules within the catalyst. Mesoporous silica materials, the main focus of this work, have controllable pore sizes and can be tailored to a specific reaction by covalent functionalization with a variety of organic functional groups in different spatial distributions. Zeolites, on the other hand, have pores that are generally too small to be functionalized covalently with organic groups. However, these materials can also become organic-inorganic hybrid catalysts of a different type when molecules are trapped within the pores and participate in reactions.

New co-condensed organic base-functionalized SBA-15 catalysts were synthesized and characterized and then demonstrated activity with a Michael reaction. These materials were then used in a Knoevenagel condensation to examine acid-base cooperativity between the amines and the silica surface hydroxyl groups. The results obtained demonstrated that acid-base cooperativity seen in the literature for isolated sites in silica gel can also be demonstrated on an extended catalytic domain on the surface of mesoporous silica, where the active sites are distributed randomly.

The focus of the zeolite study is on the hydrocarbon pool mechanism of the alcohols-to-gasoline process within the pores of H-ZSM-5. Many studies of this mechanism using methanol as the feed to this process have been done, but the hydrocarbons retained within the pores during the course of the reaction when other alcohols and alcohol mixtures are used as
feeds have not been reported in the literature. The goals of this study are to gain insight into the reaction mechanism, which is still not well understood and to see how what changes occur when different feeds are used.
Chapter 1. General Introduction

Mesoporous silicas as catalyst supports

Mesoporous silicas have emerged as a promising support for organic catalytic sites because of their characteristic high specific surface areas and tunable properties. These materials are synthesized using a micelle template around which tetraethoxysilane or tetramethoxysilane can self-assemble as it undergoes hydrolysis and condensation into a silicate structure. The resulting mesoporous (pores 20-500 Å) silica has uniform pore sizes that are larger than those that can be achieved in zeolites (less than 10 Å), which are typically microporous materials (pores <20 Å). In addition to improved mass transfer, the large pore size of mesoporous materials offers space for functionalization of the surface with a wide variety of organic groups. “One-pot” synthesis methods of mesoporous silica allow direct incorporation of a variety of organic functional groups by co-condensation while retaining structural order. Organic groups may also be immobilized on the silica surface after the structure is synthesized. Mesoporous silicas can also be used as a support for inorganic acids and bases, as well as for immobilization of enzymes or drugs. Other possible applications are adsorbents for dyes, metals, or ligands for organometallic catalysts. Whereas zeolites have been extensively used in the petrochemical industry, such catalysts are not as well-suited for production of specialty chemicals that require careful control of the catalytic domain to obtain desired chemicals while minimizing the formation of byproducts. This issue is becoming more important with the rise of interest in producing chemicals from biorenewable materials, for example, and other chemicals that are also vulnerable to alternative reaction pathways, creating challenges in yield and selectivity.
Mesoporous silicas effectively turn homogeneous catalysts into heterogeneous catalysts, which have the advantages of simplified separations downstream and the potential for better selectivity than homogeneous catalysts. The use of mesoporous silica as a support allows remarkable control of the catalytic domain, earning these materials the term “nanoreactors.” Organic-functionalized mesoporous silicas can also be used as alternatives to enzymes, which are highly specific and effective, but also are expensive and very sensitive to operating conditions.

**Types of mesoporous silica**

There is a growing variety of mesoporous silicas, including hexagonal, cubic and lamellar structures, depending on the synthesis method and the choice of micelle template. The first ordered micelle-templated silica catalysts were developed in 1992 by researchers at Mobil. These MCM-41 silicas are assembled under basic conditions using a quaternary ammonium surfactant, such as cetyltrimethylammonium bromide (CTAB), which results in a highly ordered hexagonal structure. Removal of the surfactant template requires an acid extraction or calcination. In 1996, Burkett et al. reported the synthesis of the “first examples of covalently linked, ordered hybrid inorganic-organic networks.” These catalysts were synthesized with phenyl groups or \( n \)-octyl groups using hexadecyltrimethylammonium bromide (C\(_{16}\)TMABr). Figure 1, below, is taken from a review paper by Hoffmann et al. and depicts the self-assembly process of the formation of a silica structure around a micelle template from the hydrolysis and condensation of either tetraethoxysilane or tetramethoxysilane. After formation of the silica structure, the surfactant is removed to give the final porous material.
**Figure 1.** Formation mechanism of micelle-templated mesoporous silicas.²

HMS silicas, first synthesized by Tanev and Pinnavaia and reported in *Science*¹⁶ in 1994 are assembled using a neutral surfactant such as *n*-dodecylamine. HMS silicas contain wormhole-like pores in a spongelike structure and have thicker walls than MCM-41.¹⁵⁻¹⁷ Pore size is strongly dependent on the length of the aliphatic chain, ranging from 20 to 40 Å.²,¹⁶⁻¹⁸ Although HMS silicas have structural order, MCM-41 exhibits higher long-range order than HMS silicas.¹⁸ Another difference between the two synthesis methods is that the surfactant template is easier to recover from HMS than MCM-41.¹⁸

SBA-15 silica was first developed by Zhao et al.⁵ and published in *Science* in 1998. These materials have a well-ordered hexagonal structure of pores of up to 300 Å.⁵ This type of silica is assembled under acidic conditions using the triblock amphiphilic copolymer Pluronic P123 consisting of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide), (EO)₂₀(PO)₇₀(EO)₂₀.⁵,¹⁹ The EO blocks are highly soluble in water while the PO blocks are only slightly soluble in water. Consequently, the PO segments form the micelle cores while the EO groups form the micelle/solvent interface.²⁰ Under acidic conditions, the
oxygen atoms in the EO outer blocks are protonated and form hydrogen bonds with the solvent and the silica precursors. SBA-15 is believed to be formed via a cooperative assembly of the surfactant and the silica precursor, as in Figure 1.1b, rather than via true liquid crystal templating, as shown in pathway 1.1a, where the micelles are formed in solution before the silica precursor is added. MCM-41 requires surfactant concentrations at or above the critical micelle concentration. SBA-15 also has a network of micropores of 5-15 Å in diameter, formed by poly(ethylene oxide) chains extending into the silica walls formed around the micelles; these micropores are absent from MCM-41. Mesoporous SBA-15 may be obtained using between 0.5 wt.% and 6 wt.% Pluronic P123. Syntheses using less surfactant result in amorphous silica while syntheses using larger amounts produce silica gel or do not precipitate silica. Silica gel is also produced at temperatures above 80°C. Not only does silica gel lack uniform pores, but functional groups incorporated by a one-pot synthesis method of this type are much less likely to be accessible to reactants due to incorporation of the groups within the silica structure. As with HMS, the copolymer template can be removed by refluxing in ethanol without losing the functionality of the pores. SBA-15 catalysts have pore walls of 31-64 Å, which are thicker than those of MCM-41 and HMS, thus providing increased thermal stability. The lengths of the copolymer blocks facilitate creation of pores larger than those possible in MCM-41 or HMS. Wider pores created by the large copolymer can accommodate more organic functional groups. Pore size can be varied by changing the temperature of the synthesis solution and/or the aging temperature, where increasing temperature increases the pore diameter due to the decreasing solubility of the EO blocks. Alternatively, copolymers with blocks of different lengths may also be used. Such tunable pore diameters can allow shape selectivity. In a study of the
applications of propylsulfonic acid-functionalized MCM-41, Rac et al. demonstrated the
ability to shift reaction selectivity in three systems by changing the pore diameter.\textsuperscript{28} Karam
et al.\textsuperscript{29} found that propylsulfonic-functionalized silica achieved greater selectivity of
esterification of fatty hydroxylated carboxylic acids with glycerol for amphiphilic monoesters
than homogeneous acids or other common acid catalysts. In this case, the mesoporous
catalyst had pores sufficiently large for high yield of the amphiphilic monoesters while the
restricted pore diameter prevented side polymerization reactions. The authors also claimed
that the hydrophilicity of the surface improved turnover frequencies by easing desorption of
the reaction products, which also helps inhibit the polymerization reactions.

**Silanols and surface properties**

Mesoporous silicas contain surface hydroxyl groups, known as silanols. The surface
silanol density depends on the synthesis method.\textsuperscript{30} Thermal treatment condenses adjacent
silanols to form siloxane bonds, making the surface less hydrophilic, while the curvature of
the pore determines the number and spacing of silanols.\textsuperscript{31,32} There are three types of silanols:
isolated, geminal and hydrogen-bonded. When two hydroxyl groups are bonded to the same
silicon atom, they are known as geminal silanols. Hydrogen-bonded silanols, which must be
within 3 Å of one another, are less reactive towards surface modification.\textsuperscript{33,34} Silanols can act
as Brönsted acids, hydrogen-bond donors, or hydrogen-bond acceptors. Silanols of different
acidities have also been confirmed by pyridine chemisorption followed by thermogravimetric
analysis (TGA),\textsuperscript{35} which showed two desorption peaks, one at 50-100°C for the hydrogen-
bonded silanols and one at 120-170°C for free silanols. Ong et al. used surface second
harmonic generation to study the silica/water interface and reported pK\textsubscript{a} values of 4.5 for
19% of the silanols and 8.5 for 81% of the silanols.\textsuperscript{36} This means that some silanols are more acidic than acetic acid, which has a $\text{pK}_a$ of 4.74. Silanols with greater acidity have been proposed to be the result of hydrogen bonding between two silanols, where one proton is shared between the two oxygen atoms, leaving the other proton relatively “unbonded.”\textsuperscript{34} A recent SBA-15 study with adsorption of benzylamine proposed a $\text{pK}_a$ of less than or equal to 2 for the more acidic silanols and a $\text{pK}_a$ of 8.2 for the geminal, less acidic silanols.\textsuperscript{37}

**Functionalization of mesoporous silica**

Mesoporous silicas have been functionalized with a variety of organic functional groups: acids and bases, hydrophobic and hydrophilic groups. These functional groups may be added during synthesis of the silica structure, via co-condensation, or by post-synthesis grafting after surfactant template removal, where a functional alkoxysilane reacts with silanols at the surface to anchor the organic group to the silica support. Multiple groups may be incorporated at the same time or sequentially, where co-condensation of one organic group may be followed by grafting of another. The different methods of incorporation result in different distributions of functional groups and affect the catalyst structure in different ways. These methods and the types of groups that can be incorporated into mesoporous silica are discussed in the following sections.

**Incorporation of organic groups**

Incorporation of organic acid groups, especially sulfonic acid\textsuperscript{38} and arenesulfonic acid\textsuperscript{25} groups, into mesoporous silica via co-condensation has received considerable attention. These acid catalysts are synthesized from mercaptopropyl and chlorosulfonylphenyl groups, respectively; oxidation of the thiol to the sulfonic acid group is
achieved with hydrogen peroxide, while the arenesulfonic acid is formed during synthesis from the acidic conditions. Propylthiol groups on mesoporous silica have also been used for heavy metal adsorption.\textsuperscript{11} SBA-15 mesoporous silicas containing weaker acids such as phosphonic acid from phosphonic acid diethyl ester groups\textsuperscript{39} and carboxylic acid from cyanoethyl groups\textsuperscript{40,41} have also been synthesized. The cyano group is hydrolyzed by refluxing in sulfuric acid during extraction of the micelle template.\textsuperscript{40,41} Acid groups may not be directly added to the synthesis solution because such groups would interfere with the condensation assembly process around the surfactant.

Organic bases incorporated into silica are commonly used in Knoevenagel condensation reactions,\textsuperscript{42-45} Michael additions,\textsuperscript{45,46} aldol reactions\textsuperscript{47,48} and monoglyceride synthesis,\textsuperscript{49} as well as for adsorption applications\textsuperscript{50,51} and as ligands for metal catalysts.\textsuperscript{30} The most common basic moiety incorporated into mesoporous silica is propylamine. 3-Aminopropyltriethoxysilane can be co-condensed into SBA-15, HMS or MCM-41 with tetraethoxysilane to provide a primary amine requiring no modification.\textsuperscript{43,52-56} The amine is protonated under the acidic synthesis conditions of SBA-15. In order to avoid disruption of the silica assembly around the micelle, it is necessary to allow a tetraethoxysilane prehydrolysis period of an hour or more before addition of the basic precursor.\textsuperscript{53} Aminopropyl groups may also be grafted onto silica surfaces using ammonia as a reactant, which breaks siloxane bonds, forming a new silanol adjacent to an aminopropyl group.\textsuperscript{57} Amines of higher order have also been incorporated into mesoporous silica. Cauvel et al. used 3-piperidinopropyl groups on MCM-41 to synthesize monoglycerides.\textsuperscript{49} Diamine groups have also been incorporated into SBA-15 via co-condensation and used to catalyze a Knoevenagel condensation reaction.\textsuperscript{58} Imidazole groups\textsuperscript{59} as well as derivatives of
pyridine\textsuperscript{10,51,60-62} and dihydroimidazole groups,\textsuperscript{62-64} have also been incorporated via grafting into a variety mesoporous silicas, as well as a limited number of co-condensation syntheses, but no co-condensed SBA-15 have been reported in the literature so far.

Surface silanols can inhibit catalytic activity of bases via hydrogen bonding, formation of zwitterions with primary amines, or competitive reactions. Hicks et al. used hexamethyldisilazane (HMDS) to avoid these effects with aminopropyl groups.\textsuperscript{65} Similarly, McKittrick used a tritylimine patterning agent to isolate aminopropyl groups.\textsuperscript{66} The study by Cauvel et al. mentioned above used silylation to prevent a competitive grafting reaction with the silanols during monoglyceride synthesis.\textsuperscript{49}

As interest in ionic liquids grows, some authors are supporting such groups on mesoporous silica and using these materials as catalysts. For example, Paun et al.\textsuperscript{67} grafted Hunig’s base ammonium groups onto silica gel and Liu et al.\textsuperscript{68} co-condensed 1-methyl-3-propylimidazolium and 1-propylpyridinium into SBA-15 for use in Knoevenagel condensations.

Chiral groups may be incorporated for enantioselective catalysis, often by grafting or post-synthetic modification of co-condensed groups for an organometallic catalysis, a rapidly growing area of interest.\textsuperscript{12,69-71}

Hydrophobic or neutral groups, such as methyl, ethyl and phenyl groups, can be incorporated into silica catalysts to shift reaction selectivity toward nonpolar reactants.\textsuperscript{72} Nonpolar groups can be used to exclude water from the active sites for condensation reactions and other reactions inhibited by water.\textsuperscript{72} Mbaraka and Shanks incorporated hydrophobic groups by grafting as well as co-condensation with SBA-15 sulfonic acid groups in order to exclude water from the pores for the catalysis of fatty acid esterification.\textsuperscript{72}
Addition of organic groups by co-condensation or by grafting can alter the hydrophilicity or hydrophobicity of the catalyst surface, thereby affecting dispersion of the catalyst in a solvent or influencing the partitioning of reactants near the catalyst surface. Huh et al. incorporated hydrophobic groups along with 3-[(2-aminoethylamino)ethylamino]propyl groups into mesoporous silica nanospheres to shift selectivity of a competitive aldol reaction to favor a nonpolar reactant.73

**Grafting vs. co-condensation**

The most common functionalization methods of mesoporous silica are grafting and co-condensation. In co-condensation, a functional silane is added to the catalyst synthesis mixture so that it is incorporated into the silica framework in situ. Grafting, the post-synthesis method of incorporating the same groups, is usually carried out in a nonpolar solvent in order to increase the favorability of the grafting group for the surface silanols. One drawback of co-condensation is that these materials cannot be calcined for removal of the micelle template, common for MCM-41.47 Mass transfer limitations during grafting can focus the functional group into deposits on the exterior of the particle and at the pore openings.72,74 However, in co-condensation, the functional groups are mostly within the pores due to preference for the micelles, resulting in a more uniform distribution than grafting.75 This has been demonstrated by Fiorilli et al. with SBA-15 functionalized with carboxylic acid groups using infrared spectroscopy.76 Additionally, Lim and Stein contrasted clustering of vinyl groups at pore mouths from grafting with greater dispersion via co-condensation using MCM-41.74 Further support of this trend comes from a study by Mbaraka and Shanks,72 where a hydrophobic group was co-condensed with propylsulfonic acid into SBA-15 for the purpose of excluding water from the catalytic acid sites within the pores.
during the esterification of fatty acids with methanol. The authors observed that grafting methyl, ethyl or phenyl groups rendered the particles hydrophobic and incapable of being dispersed in water, while synthesis by co-condensation of the same hydrophobic groups retained the particles’ hydrophilicity, as depicted in Figure 2, below.

![Figure 2. Distribution of hydrophobic organic functional groups from A) grafting and B) co-condensation.](image)

Co-condensation generally affords greater control over the extent of functionalization, determined by the amount of functional silane added during the one-pot synthesis. Increasing loading can reduce structural order as the functional silane condenses with itself; consequently, co-condensed functional group loadings are generally kept at or below 40 mole %. Grafting, on the other hand, can produce much higher functionalization, up to full surface coverage. However, the number of functional groups added depends on the number of surface silanols. Calcination of silicas for template removal creates hydrophobic regions by dehydroxylation of the surface, resulting in clusters of grafted groups. Grafting usually reduces the pore diameter and specific surface area; as the pore opening narrows, diffusion of the functional silane deeper into the pores is inhibited. Pores can become
completely blocked when trace levels of water during grafting lead to polymerization of the grafting precursor with itself. Additionally, some grafted moieties are less stable than co-condensed moieties because, while co-condensed groups are anchored in the silica framework, grafted groups can lack complete condensation of all three hydroxyls. As a result, for example, aminopropylsilane is more likely to leach into solution when grafted onto the surface, catalyzing its own hydrolysis in aqueous solution. The extension of the grafted group from the surface gives the moiety greater mobility and ability to form hydrogen bonds with its own uncondensed silanols or surface silanols as well as with other amines. Some of these interactions that can reduce the catalytic activity of primary amines are shown below in Figure 3. Spectroscopic studies by Brunel et al. indicated that the number of co-condensed amines in zwitterions is higher in grafted materials than co-condensed materials; an estimated 40% of grafted aminopropyl groups interact strongly enough with silanols to form zwitterions.

![Figure 3](image.png)

**Figure 3.** Possible interactions between grafted primary amines and silica surface silanols.

Moieties that may undergo unfavorable reactions in the synthesis mixture or interfere with the self-assembly process by disrupting the surfactant micelles may be obtained by post-synthesis removal of a protecting group as an alternative to grafting the final structure onto the surface. This method is known as imprinting and will be discussed in the next section.
**Controlled functionalization by imprinting**

Well-defined sites within silica can be obtained using an imprinting method. Imprinting has been developed by Katz et al. to control positioning of organic functional groups within silica gel and isolate functional groups.\(^1,81-84\) In this type of functionalization method, an organic scaffold is incorporated into the silica with tetraethoxysilane during acid-catalyzed sol-gel synthesis.\(^1\) Part of the organic scaffold is subsequently removed, leaving behind two or three functional groups at fixed distances apart. This is known as thermolytic deprotection, where the imprint is removed from the supported group, usually by cleavage of a carbamate group, as shown in Figure 4.\(^1,42,81-84\) These authors have synthesized materials with various functionalities: two thiol groups with an aminopropyl group,\(^82\) two amines,\(^83\) three amines,\(^1\) and a proline catalyst with the potential for use as a chiral catalyst.\(^81\) Microporosity of 5-10 Å is common to bulk imprinted materials,\(^1,81\) although Bass and Katz obtained a mean radius of 32 Å in their aminopropyl-functionalized material. While this method offers control of the catalytic environment, the amorphous
character of these silica gels also means that the active sites successfully imprinted are not necessarily all accessible to reactants.

**Cooperative catalysis**

When two or more active sites acting through either concerted or successive separate mechanisms catalyze a reaction, this behavior is referred to as cooperative catalysis.\(^5\) This cooperativity can result in higher activity than that of the individual sites and can also affect reaction selectivity. As the goal of this project is the synthesis and catalytic testing of a cooperative catalyst with controlled spacing of the organic moieties, a brief literature review is discussed below.

**Enzyme acid-base pairs**

Cooperative catalysis is epitomized by enzymes, which employ multiple groups when catalyzing a reaction. Many enzymes utilize amino acid pairs in their active sites in acid-base cooperative mechanisms. Glycoside hydrolase active sites, like those in cellulases, usually consist of a protonated glutamic acid or aspartic acid residue and a glutamate or aspartate residue.\(^6\) The key differences between enzymes and synthetic catalysts, which may contain the same catalytic residues, are that the structure of an enzyme isolates the active site from its surroundings, maintaining the desired pH, and also distorts the substrate, straining intramolecular bonds, making the substrate more reactive.

**Cyclodextrins, polymers, and other enzyme mimics**

Cooperative catalysis has been demonstrated with functionalized cyclodextrins and other polymers used as enzyme mimics. Such materials may be desirable when the use of enzymes is prohibited by cost or operating conditions. Cyclodextrins are rings of glucose
units with hydroxyl groups that can function as attachment sites for organic groups such as imidazoles, allowing control of spacing. An interesting property of cyclodextrins is that the inside of the ring is more hydrophobic than the outside of the ring, due to the positioning of the hydroxyl groups on the exterior. As a result, cyclodextrins have even been incorporated into mesoporous silica for the removal of organic compounds from water. Cooperative catalysis by enzyme mimics in aqueous solutions requires a buffer to maintain the desired site protonation. In general, acid-base cooperativity between imidazole sites is achieved when the solution pH is equal to the pKₐ of the imidazole group, which is the peak of a bell-shaped reaction rate curve, when the number of acids and bases are equal. Nilsson and Baltzer achieved similar results for the hydrolysis of nitrophenyl esters in a buffered solution with a polypeptide catalyst with an active site consisting of a pair of histidine residues where one of the residues is protonated.

Polymers have also been used as supports for various catalytic groups. For example, Overberger and Maki compared the activities of copolymers of 4(5)-vinylimidazole and vinylsulfonic acid with 4(5)-vinylimidazole and acrylic acid for esterolytic reactions. Whereas the copolymers with vinylsulfonic acid were inactive, the polymers with the carboxylic acid and imidazole groups displayed cooperativity with a bell-shaped plot. Baker et al. synthesized poly(propylene imine) dendrimers with imidazole moieties to catalyze the hydrolysis of 2,4-dinitrophenyl acetate. Even with a variance in pH, the authors were unable to achieve cooperative catalysis, finding instead that activity increased with increasing pH, most probably due to too large of spacing between imidazole groups.
**Acid-base bifunctional silica catalysts**

There are many acid-base bifunctionalized heterogeneous catalysts presented in the literature. The vast majority of these use metals as active sites, often where acidic catalysts are doped to adjust the acidity. Weak acids can work well with weak bases in a concerted mechanism and may be favored over a single strong acid or base for easier desorption of reaction products. One class of acid-base catalyst is that of Mg-Al mixed oxides, where the acidity and basicity are determined by the molar ratio of Mg:Al and by the synthesis conditions. These materials have Lewis acid, Lewis base and Brönsted base sites that can act in concert or successively in aldol condensations, Knoevenagel condensations and Michael reactions.

Organic acids and bases have been incorporated into silica as effective bifunctional catalysts. A catalyst system of acids and bases “entrapped” in silica gel has been used as a “one pot” catalyst system for simultaneous sequential reactions by Gelman et al. The authors incorporated Nafion perfluorinated sulfonic acid resin and diamine or guanidine base groups separately into sol-gel silica and used the mixture for an acid-catalyzed pinacol-pinacalone rearrangement, followed by a base-catalyzed condensation reaction. However, resins require solvation for their porosity, are not structurally ordered and are not thermally stable.

Chang and Liu grafted dihydroimidazole, isobutyl, carboxyl and ethylenediamine groups onto SBA-15 silica as an chymotrypsin enzyme mimic. Although the catalyst was active in the hydrolysis of a phenyl ester, a buffer was required. The authors also found that the reaction rate decreased with increasing surface coverage due to a decrease in pore diameter by 20 Å from the grafting reaction.
Huh et al. synthesized mesoporous silica nanospheres with an ureidopropyl group, which can function as a general acid, and a 3-[2-(2-aminoethylamino)ethylamino]propyl group as a base. These bifunctionalized particles were used to catalyze aldol, Henry and cyanosilylation reactions. Stronger acids have been incorporated into mesoporous silica by Zeidan et al., who co-condensed aminopropyl and arenesulfonic acid groups into SBA-15 silica and demonstrated catalytic activity in the aldol condensation of acetone and 4-nitrobenzaldehyde. The authors extended this study to phosphoric acid and carboxylic acid groups, finding that the carboxylic acid groups generated the highest catalytic activity when co-condensed with aminopropyl groups.

In a study involving catalytic testing and computational modeling of the dehydrocondensation of methanol and isobutanol into methyl isobutyl ether and dimethyl ether, Herman et al. proposed cooperativity between adjacent sulfonic acid groups immobilized on SBA-15, where one of the acids in each pair functions as both an acid and a base.

Motokura et al. recently grafted amine groups onto amorphous silica-alumina for the catalysis of a cyano-ethoxycarbonylation reaction, a Michael reaction, and nitro-aldol reactions. The authors claimed to observe cooperative catalysis between the amine and the strong Bronsted acids on the surface of the support. A mixture of unfunctionalized amorphous silica-alumina and an unsupported amine achieved an initial rate of 2.44 mmol/h for a cyano-ethoxycarbonylation reaction, while the functionalized support achieved an initial rate of 2.73 mmol/h. Interestingly, when either moiety was weakened, by replacing a secondary amine with a primary amine or by using silica as the support for the secondary amine, the initial rate was significantly lower: 0.51 mmol/h. This result stands in contrast to
the results of Zeidan,\textsuperscript{101,102} where a weaker acid group was more catalytically active than a stronger acid when paired with an amine, as well as common enzyme mimetics, which usually employ amino acid groups as weak acids and bases.\textsuperscript{105} When Motokura et al. used primary amines in a nitro-aldol reaction, the amine-grafted silica-alumina was much more active than the homogeneous amine or the mixture of amine and support, which had the same activity.\textsuperscript{104} In this case, the mixture of homogeneous amine and unfunctionalized silica-alumina did not display cooperativity.

\textbf{Dissertation organization}

The study of organic-functionalized mesoporous silicas is divided into two chapters, following an introduction to these materials in Chapter 1. Chapter 2 discusses the synthesis, characterization, and catalytic testing of new amine-functionalized catalysts. These catalysts are then used in a study of acid-base cooperativity in Chapter 3. The fourth chapter covers work done the alcohols-to-gasoline reaction using the zeolite H-ZSM-5 with a focus on the hydrocarbon pool mechanism. This work was done in the summer of 2008 at the Center for Sustainable and Green Chemistry at the Technical University of Denmark (DTU), through a Partnerships for International Research & Education program funded by the National Science Foundation. A portion of this work at DTU was published in a co-authored article that is included in the Appendix. Another co-authored publication included in the Appendix is from a collaboration with the Chandler group at Trinity University that discusses an assay that was developed for the characterization of amine-functionalized mesoporous silica catalysts. The other two chapters included in the Appendix discuss work that did not lead to publications. One of these chapters is about the original goal of cooperative catalysis using bifunctional
catalysts with controlled spacing between the moieties as part of a collaborative effort that encountered difficulties with the chemical synthesis. The other chapter discusses the challenges of a study intending to examine the relationship between basicity and catalytic activity.

References

(9) Yan, Z. T., Shengyang; Yin, Jinxiang; Li, Guangtao J. Mater. Chem. 2006, 2347-2353.


A paper to be submitted to the Journal of Molecular Catalysis

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Abstract

Mesoporous silica functionalized with organic groups is a catalyst class of great potential currently receiving considerable attention. In the work discussed here SBA-15 silica catalysts with pyridine and dihydroimidazole groups have been synthesized and the catalytic activities of these materials were demonstrated with a Michael addition reaction. The organic functional groups were incorporated via co-condensation and characterized for the first time. Unlike previous materials reported in the literature with these functional groups, these have highly accessible extended surfaces within the pores that can serve as catalytic domains, with a more uniform distribution of active sites than catalysts functionalized by grafting.

Introduction

A range of functional group basicity is desired for design of bifunctional acid-base catalysts, where a stronger base is not necessarily better. For example, Zeidan and Davis showed that the co-condensation of an acid with an aminopropyl group had increasing catalytic activity with decreasing strength of the acid, from arenesulfonic acid to phosphoric
acid to carboxylic acid, which displayed the highest activity, as the acid and base groups were least likely to form zwitterions when the acid was weak. Additionally, different bases can catalyze a reaction via different mechanisms, as with the Knoevenagel condensation, for example. The mechanism through which a catalyst proceeds can determine selectivity for a reaction. Consequently, a variety of bases is desired from which a moiety can be selected when designing a controlled reaction domain in mesoporous silica.

Aminopropyl groups are the most commonly studied of the organic bases that have been supported on silica. Although this functional group is an effective base catalyst, it tends to interact with surface silanols and other nearby amines through hydrogen bonds or zwitterions. Such interactions can reduce the catalytic activity of these materials. This is especially the case when added via grafting, where grafted aminopropyl groups have been shown to be incorporated in clusters or “aminopropyl islands.” Additionally, if a bifunctional acid-base catalyst is desired, primary amines in close proximity to carboxylic acid groups can react to form amide bridges. Such instances make having alternative bases from which to choose an attractive option. The rings of the pyridine and dihydroimidazole restrain the mobility of the basic nitrogen and provide steric hindrance, making these groups less vulnerable to these problems common with aminopropyl-functionalized silicas. In the work described here, derivatives of pyridine and imidazole have been incorporated into SBA-15 mesoporous silica by co-condensation. The Michael reaction of nitrostyrene and malononitrile was used for catalytic testing. All three bases are expected to operate via the same mechanism: the base moiety abstracts a proton from the malononitrile molecule, forming a carbanion intermediate, which can then be added to nitrostyrene at the double bond. The carbanion is likely to be partially stabilized by hydrogen bonding with an
adjacent silanol. The steps of the mechanism with the postulated participation of the surface silanols is depicted in Figure 1.

![Diagram](image)

**Figure 1.** Postulated Michael reaction mechanism steps. A) Base group deprotonates malononitrile, forming a carbanion, which is stabilized by a hydrogen bond with a neighboring silanol. B) Carbanion undergoes nucleophilic attack on trans-β-nitrostyrene. C) Product is formed and catalyst base group returns to its initial state.

SBA-15 mesoporous silica was first developed by Zhao et al., as reported in *Science* in 1998. This type of silica is assembled under acidic conditions using the triblock amphiphilic copolymer Pluronic P123, which consists of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide), (EO)$_{20}$(PO)$_{70}$(EO)$_{20}$. These materials have a well-ordered hexagonal structure of pores of up to 300 Å. Pyridine has been
incorporated via co-condensation into HMS and has been grafted onto SBA-15 and HMS silica.\textsuperscript{33-36} HMS silicas are synthesized using a neutral surfactant, typically \textit{n}-dodecylamine, and have pore sizes ranging from 20 Å to 40 Å.\textsuperscript{37,38} Using SBA-15, the larger pores can accommodate larger organic groups. Yan et al. used a modified version of pyridine, one linked to an amide group and used the resulting co-condensed SBA-15 silica as an adsorbent for acid dyestuffs.\textsuperscript{34} The aromaticity of pyridine results in less electron density at the nitrogen atom, resulting in a weaker base, with a homogeneous pK\textsubscript{b} of 8.75.\textsuperscript{39} Propylamine, on the other hand, is a stronger base, with a homogeneous pK\textsubscript{b} of 3.32.\textsuperscript{39} The lack of aromaticity along with resonance stabilization of the protonated form gives the dihydroimidazole group the strongest basicity of these three. Markowitz et al. modified silica particles with amine and dihydroimidazole groups and carried out titrations with Hammett indicators.\textsuperscript{40} The authors found that the dihydroimidazole groups appeared to be stronger basic sites than \textit{N}-(3-aminoethylaminomethyl)-phenyl groups, determined by the bromothymol blue indicator (H\textsubscript{=} = 7.2).\textsuperscript{40} Dihydroimidazole groups have also been used for adsorption of metals on a sol-gel silica support.\textsuperscript{41} Dihydroimidazole groups have been co-condensed into cubic cage-like SBA-16 and FDU-1 silica, which have nonuniform pore entrances when functionalized.\textsuperscript{42} Burleigh et al. synthesized periodic mesoporous organosilicas with dihydroimidazole and pyridine groups by co-condensation, using bis(triethoxysilyl)ethane as the silica precursor and cetyltrimethylammonium chloride as the surfactant.\textsuperscript{43} These silicas had pore diameters of 27 Å or less.\textsuperscript{43}

Co-condensation of functional silanes with tetraethoxysilane (TEOS) has been shown to create a better distribution of organic functional groups than post-synthesis grafting methods.\textsuperscript{44,45} Although a higher amount of organic groups can be incorporated via grafting,
the loadings are more controllable in co-condensation. Most grafting agents contain three ethoxy or methoxy groups that undergo hydrolysis and condensation, accordingly reducing the number of silanols, which may function as weak acids or participants in hydrogen-bonding. The decrease of the number of silanols due to grafting of \( N-(3-\text{triethoxysilylpropyl})4,5\)-dihydroimidazole was observed by Kang et al., where FTIR of the samples after grafting shows a significant reduction in the silanol band at 3600 -3200 cm\(^{-1}\). An additional consequence of complete coverage by grafted groups and the loss of silanols is a reduction in hydrophilicity of the catalyst surface.

**Experimental**

**Catalyst synthesis**

The synthesis procedures described here have been adapted from the synthesis of co-condensed aminopropylated SBA-15. All chemicals were used without further purification. The structure-directing agent, Pluronic P123 (BASF Co.), (4 g) was dissolved in 125 ml deionized water and 25 ml hydrochloric acid (12.1 N). Tetraethoxysilane (TEOS) was added as the silica precursor (98%, Acros Organics) at 40°C. The functional silane, either 3-aminopropytriethoxysilane (APTES), 2-(trimethoxysilylethyl)pyridine (TMED), or \( N-(3\text{-triethoxysilylpropyl})4,5\)-dihydroimidazole (TEDH), was added after a TEOS prehydrolysis period of one hour. These organosilanes were purchased from Gelest and their structures are shown in Figure 2. A period of time for the hydrolysis of tetraethoxysilane before the functional silane is added is necessary to retain structural order, since positive block copolymer micelles. However, if this prehydrolysis period is too long, the functional silanes are less likely to all be incorporated into the catalyst structure. The
resulting mixture (1 TEOS: 0.1 APTES/TMEP/TEDHI: 7.76 HCl: 171 H$_2$O molar ratio) was stirred at 40°C for 20 h and aged at 90°C for 24 h before being filtered. The surfactant template was removed by refluxing in ethanol with 10 wt.% hydrochloric acid for 24 h. The catalyst was then filtered and washed with ethanol. The resulting catalysts were named APS, EPS, and DHIS, respectively. Excess protons from the acidic synthesis conditions were removed with 5 ml tetramethylammonium hydroxide (TMAH) solution (25 wt. % in methanol, Acros Organics) in 45 ml methanol with stirring for 30 min, followed by filtration and three washes with methanol.

**Catalyst characterization**

Nitrogen adsorption/desorption was performed at -196°C with a Micromeritics ASAP 2000 system to obtain BET specific surface areas and BJH pore size distributions. Thermogravimetric analysis of silylated and unmodified APS was performed with a Perkin-Elmer TGA7 for identification and quantification of functional groups using a nitrogen purge and a temperature ramp of 5°C/min before and after holding at 120°C for ten minutes. The weight percent of nitrogen in the catalyst was determined by elemental analysis using a
Perkin-Elmer Series II 2400 CHN analyzer. Powder x-ray diffraction analysis was done using a Scintag XDS 2000 diffractometer with a Cu-Kα radiation source in the region of 1° to 10° 2θ with a step scan rate of 0.04°/min. Fourier transform infrared spectroscopy (FTIR) transmission data were collected for pellets made with potassium bromide using a Nicolet 6700 FT-IR (Thermo Electron Corp.).

$^{29}$Si (59.62 MHz) solid-state magic-angle spinning NMR spectra were obtained using a 300 MHz wide-bore magnet with a TecMag Discovery console and a Chemagnetics double-channel 7.5 mm pencil MAS probe (spinning speed of 5 kHz). In all of the experiments 0.2 g of sample was used to load the rotor. Each single-pulse spectrum was acquired by signal-averaging 2000 scans with a 60 s pulse delay.

**Catalytic testing**

The Michael addition of malononitrile and trans-β-nitrostyrene was performed at 25°C under nitrogen with benzene as the solvent. A small amount of toluene was added as an internal standard. Samples were taken via syringe and analyzed using a Varian gas chromatograph (CP-3800) with a Varian CP7417 column and a flame ionization detector.

**Results and discussion**

**Catalyst characterization**

Nitrogen adsorption/desorption data indicate uniform median diameters of 55 Å to 60 Å. All materials displayed sharp adsorption and desorption isotherms of the same shape, consistent with narrow pore size distributions.$^{49}$ These results are shown in Figure 3 and Table 1. These hysteresis loops correspond to type H1, consistent with the uniform size and shape of the pores.$^{50}$ These isotherms are of type IV, where a sharp adsorption volume
increase occurs upon capillary condensation of nitrogen in the mesopores. The isotherms for the aminopropyl-functionalized silica (APS) are almost identical to those for the pyridine-functionalized material (EPS); the isotherms for the dihydroimidazole-functionalized silica (DHIS) are shifted below these, corresponding to the reduced specific surface area, but no structural change. The pore size distribution also indicates the presence of micropores that are typical for SBA-15. The nitrogen adsorption/desorption are shown in the table below, along with the elemental analysis results. Although the DHIS catalyst had a lower specific surface area than the APS and EPS catalysts, elemental analysis results indicated similar loadings per gram of catalyst. The consistency of pore diameters and amine base loadings allow the materials to be catalytically tested without having to account for any significant differences in mass transfer resistance.

Table 1. Nitrogen adsorption/desorption data and catalyst loadings

<table>
<thead>
<tr>
<th></th>
<th>Surface area m²/g</th>
<th>Median pore diameter Å</th>
<th>N content mmol/g</th>
<th>% Si functionalized b</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>655</td>
<td>57.5</td>
<td>0.93</td>
<td>8.2</td>
</tr>
<tr>
<td>DHIS</td>
<td>580</td>
<td>56.5</td>
<td>0.93</td>
<td>8.9</td>
</tr>
<tr>
<td>EPS</td>
<td>670</td>
<td>57.5</td>
<td>0.96</td>
<td>8.4</td>
</tr>
</tbody>
</table>

a From BJH adsorption
b From ²⁹Si MAS NMR
Figure 3. a) BJH adsorption pore size distributions for APS (+), EPS (○), and DHIS (×). b) Nitrogen adsorption/desorption isotherms for aminopropyl-functionalized silica (AP), pyridine-functionalized silica (Py), and dihydroimidazole-functionalized silica (DHI).

Powder X-ray diffraction results contained a single strong peak corresponding to the (100) plane and smaller secondary peaks corresponding to the (110) and (200) planes. These results for the 10% functionalized dihydroimidazole and pyridine catalysts are shown in Figure 4. Figure 4c also shows the lack of peaks for completely amorphous silica. Figure 4c shows the (110) peak at a d spacing of 58.9 Å and the (200) peak at a d spacing of 51.9 Å. These peaks are consistent with a mesoscopic one-dimensional p6mm hexagonal symmetry, as seen in the aminopropyl-functionalized and other organic-functionalized SBA-15 materials. These functionalized SBA-15 materials are not as ordered as unfunctionalized SBA-15, as indicated by the lack of the well-resolved (210) reflection and weak peaks at (300), (220) and (310) initially reported by Zhao et al.
Figure 4. Powder X-ray diffraction of a) dihydroimidazole-functionalized SBA-15 (10% loading), b) pyridine-functionalized SBA-15 (10% loading)
Figure 4c. Powder X-ray diffraction. a) Pyridine-functionalized SBA-15, 10%; b) Dihydroimidazole-functionalized SBA-15, 10%; c) Amorphous silica.

Thermogravimetric analysis results displayed three peaks for the pyridine- and dihydroimidazole-functionalized SBA-15. These results are shown in Figure 5. The first large peak is due to loss of physisorbed water and the second is due to condensation of neighboring surface silanols, forming siloxane bonds, centered around 200°C. The third peak is due to decomposition of the organic functional group, with a maximum rate of weight lost centered around 300°C for the aminopropyl group, 375°C for the dihydroimidazole group and 540°C for the pyridine group. The aminopropyl weight loss at 300°C is consistent with the literature. Weight loss above 500°C is likely due to dehydroxylation of the silica surface or decomposition of residual ethoxy groups from incomplete TEOS or functional silane hydrolysis. TGA results of unfunctionalized SBA-15 indicate that TMAH treatment
removes some of the Pluronic P123 left after extraction, but it is unclear how much is removed from base-functionalized materials, which have less surfactant remaining after synthesis. The thermal decomposition pathway established in the literature for aminopropyl groups on silica is shown in Figure 6a.\textsuperscript{54} The propylamine group condenses with a neighboring silanol and is then further decomposed into ammonia and propane.\textsuperscript{54} The aromatic pyridine ring appears to stabilize the moiety, shifting the decomposition temperature to a higher value than those for the other two bases. This moiety is believed to
Figure 5. Thermogravimetric analysis results. a) Derivative weight, b) Sample weight percent. I) DHIS, II) EPS, III) APS.
break from the silica surface, forming a double bond on the ethyl group as shown in Figure 6b. The dihydroimidazole moiety, on the other hand, lacks the aromaticity of the pyridine ring but, as a secondary amine, is less reactive with surface silanols than the primary amine. Consequently, the thermal decomposition temperature peak for this moiety lies between those of the other two moieties.

Figure 6. Thermal decomposition. a) aminopropyl groups, b) pyridine groups. Adapted from Alekseev and Zaitsev.
FTIR spectroscopy was used to identify certain bonds, thereby confirming incorporation of the organic functional groups into the SBA-15 structure. In addition to the three amine catalysts, unfunctionalized SBA-15 was also analyzed for comparison. These results are shown in Figures 7 and 8. The unfunctionalized sample contained more residual Pluronic P123 than the functionalized silicas, as indicated by an O-CH\textsubscript{2} stretching band at 1460 cm\textsuperscript{-1} and a wag band at 1380 cm\textsuperscript{-1}.\cite{55} This sample had a water adsorption peak around 1630 cm\textsuperscript{-1}.\cite{55} Spectra of aminopropyl-functionalized SBA-15 have been established in the literature, allowing comparisons to the pyridine- and dihydroimidazole-functionalized silicas.\cite{8} The primary amine can be identified by the symmetric -NH\textsubscript{3}\textsuperscript{+} deformation around 1510 cm\textsuperscript{-1}.\cite{55} The silica support produces a very strong siloxane (Si-O-Si) stretching peak at 1100-1000 cm\textsuperscript{-1},\cite{33,55} drowning out expected C-N stretching vibrations around 1000 - 1200 cm\textsuperscript{-1}.\cite{8} A similar effect with the broad silanol band prevents observation of the N-H stretching peaks expected at 3370 cm\textsuperscript{-1} and 3350 cm\textsuperscript{-1}.\cite{8,56} Adsorbed water also adds to the size of the NH bend peaks at 1620 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1}, as well as the -NH\textsubscript{3}\textsuperscript{+} antisymmetric deformation band expected at 1580 cm\textsuperscript{-1}.\cite{8,56} There is also a C-N stretching peak present at 800 cm\textsuperscript{-1}.\cite{55} The pyridine functional group is substituted at the second atom, for which (-C=N-) quadrant stretches are expected at 1633 and 1575 cm\textsuperscript{-1}, which are obscured by the adsorbed water peak.\cite{55} However, peaks are apparent at 1540 and 1475 cm\textsuperscript{-1}, corresponding to the C=C and C=N bonds, respectively, of the pyridine ring.\cite{43} The pyridine ring also has a quadrant stretch at 1575 cm\textsuperscript{-1} and a semicircle stretch at 1450 cm\textsuperscript{-1}.\cite{55} For the dihydroimidazole group, a sharp (-C=N-) absorption peak is present at 1630 cm\textsuperscript{-1},\cite{33} significantly taller and sharper than the peaks at similar wavenumbers from the APS and EPS catalysts. The N-H stretch expected around 3200 cm\textsuperscript{-1} is hidden by the broad silanol band.\cite{57}
Figure 7. FTIR spectra. a) Dihydroimidazole-functionalized SBA-15, b) Pyridine-functionalized SBA-15.
Figure 8. Partial FTIR spectra. (a) DHIPS, (b) EPS, (c) APS, (d) unfunctionalized SBA-15.
Functionalization of SBA-15 with the organosilanes was confirmed with $^{29}$Si MAS solid-state NMR. The NMR spectra are shown in Figure 9. The spectra show $Q^4$ Si, $Q^3$ Si and $T^3$ peaks at $\delta = -113$, $\delta = -104$ and $\delta = -68$ ppm, respectively, where $Q^n = \text{Si} (\text{OSi})_n (\text{OH})_{4-n}$, $n = 2, 3, 4$ and $T^m = \text{RSi} (\text{OSi})_m (\text{OH})_{3-m}$, $m = 1, 2, 3$. The $Q$ peaks correspond to siloxanes (($\text{SiO})_4\text{Si}$, $Q^4$) and single silanols (($\text{SiO})_3\text{SiOH}$, $Q^3$). $Q^2$ peaks, indicating geminal silanols, could not be effectively distinguished from these spectra, which is more likely to be due to noise in the signal than due to a complete lack of this type of silanol. The presence of the $T^3$ peaks confirms the incorporation of the organosilanes into the SBA-15 structure. $T^2$ peaks also could not be effectively distinguished from the spectra. However, it was expected that the $T^3$ peak would be dominant due to anchoring within the SBA-15 wall rather than on the surface, as more commonly found with grafted organosilanes, which are not as

![Figure 9. Solid-state $^{29}$Si MAS NMR: a) aminopropyl SBA-15, b) Dihydroimidazole SBA-15, c) Pyridine SBA-15.](image)
well-anchored. The percentages of organic-functionalized silicon atoms were calculated from ratios of the integrated areas of the T and Q peaks and are shown in Table 1. These functionalization percentages are slightly lower than the 10 molar % amounts of organosilanes added to the catalyst synthesis mixture. This suggests that most, but not all of the organosilanes are incorporated into the SBA-15 catalyst structure. The incomplete incorporation of the organosilanes is similar to the incorporation ratio of around 80% reported in the literature for 10% aminopropyl-functionalized SBA-15.\textsuperscript{47} The loadings of the pyridine and dihydroimidazole groups calculated from elemental analysis of the three catalysts are consistent with those of other organic-functionalized mesoporous silicas using 10% molar organosilanes.\textsuperscript{47}

**Catalytic testing**

All three base-functionalized mesoporous silicas were active in the Michael reaction. This testing was done at 25°C to minimize the effect of mass transfer on the measured reaction rates. The conversion of malononitrile for each catalyst is shown in Figure 10. These results are consistent with the conversions obtained by Bass et al.\textsuperscript{6} using aminopropyl-functionalized silica gel. The dihydroimidazole and aminopropyl SBA-15 catalysts were slightly more active than the pyridine SBA-15. However, there was no significant difference in the activities of the DHIS and APS catalysts. The turnover numbers for the DHIS, APS and EPS were 30.1, 30.7, and 26.8 mol/site/hr, respectively, using the loadings determined by elemental analysis. Although one might have expected the DHIS catalyst, as the strongest base, to have the highest activity of the three, the difference in basicity between the dihydroimidazole moiety and the aminopropyl moiety does not appear to affect the rate of the Michael reaction. The pyridine catalyst appears to be the least active of the three, but t-tests
Figure 10. Conversion of malononitrile in the Michael reaction at 25°C in benzene by DHIS (+), APS (○), EPS (■).

Table 2. Catalytic activities in the Michael reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Turnover number (mol/site/hr)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminopropyl SBA-15</td>
<td>30.7 ± 3.9</td>
<td>12 ± 4</td>
</tr>
<tr>
<td>Dihydroimidazole SBA-15</td>
<td>30.1 ± 2.3</td>
<td>11 ± 4</td>
</tr>
<tr>
<td>Ethylpyridine SBA-15</td>
<td>26.8 ± 4.1</td>
<td>18 ± 6</td>
</tr>
</tbody>
</table>

*Error represents 95% confidence level

using a 95% confidence interval indicated that the activity of the pyridine catalyst is not significantly different, statistically, from the activities of the aminopropyl and dihydroimidazole catalysts. Apparent activation energies were calculated for the three catalysts: 11 kJ/mol for DHIS, 12 kJ/mol for APS and 18 kJ/mol for EPS, which differ within
experimental error. These apparent activation energies are low for a carbon-carbon bond forming reaction, so it is possible that mass transfer limitations may play a role in the observed activity of these heterogeneous catalysts. The similar activities do not appear to be the result of external mass transfer limitations, since variation of the stirring rate did not affect the observed reaction rates. Consequently, to determine whether internal mass transfer limitations may be present, a Weisz-Prater number was estimated using Equation 1:  

$$N_{wp} = \frac{-r'_{A}(obs)\rho_{p}R^2}{D_{e}C_{As}}$$  

The density of the catalyst particle, $\rho_{p}$, is estimated to be 1300 g/L for SBA-15. $R$ is the catalyst particle diameter, estimated to be 2 µm. The observed reaction rate is $r'_{A}(obs)$, moles of $A$ reacted per gram catalyst per time. $C_{As}$ is the reactant concentration in the bulk, equal to the concentration at the surface, assuming no external mass transfer limitations. $D_{e}$ is the effective diffusivity, estimated as $3 \times 10^{-9}$ m$^2$/s, a value reported in the literature for the self-diffusion coefficient of ethylbenzene within MCM-41 at 25°C. Using these values, a Weisz-Prater number of 0.0002 was calculated. Since this value is much less than unity, this value indicates that there are no concentration gradients within the catalyst particles and the reaction rate is not limited by internal mass transfer. The pore diameter of the MCM-41 used in that study was 14 Å, as opposed to the 57 Å pore diameter of the SBA-15 materials used in this study, so the diffusion coefficient of nitrostyrene in toluene within SBA-15 would not likely be significantly smaller. However, if a diffusion coefficient of $D_{e} = 10^{-11}$ m$^2$/s were used, the Weisz-Prater number would be 0.05, which is still below the criterion for internal diffusion limitations.
Conclusions

Pyridine-functionalized SBA-15 and dihydroimidazole-functionalized SBA-15 were synthesized via co-condensation. Characterization of these materials revealed structural order consistent with other organic-functionalized SBA-15 mesoporous silicas. Having consistent structure with similar organic base loadings allows the comparison of different base catalysts without having to account for differences in mass transfer in the pores of the catalyst. The pyridine-functionalized silica and the dihydroimidazole-functionalized silica were tested with a Michael addition reaction and are catalytically active. The successful syntheses of these materials now provide two additional options when designing base or acid-base catalysts.

References

(29) Han, L.; Ruan, J.; Li, Y.; Terasaki, O.; Che, S. Chem. Mater. 2007, 19, 2860-2867.
Chapter 3. Acid-Base Cooperativity in Condensation Reactions with Functionalized Mesoporous Silica Catalysts

A paper accepted by the *Journal of Catalysis*

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Abstract

The Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was used to test the acid-base cooperativity of SBA-15 mesoporous silica co-condensed with aminopropyl groups as well as silica co-condensed with dihydroimidazole groups. Surface silanols were capped with trimethylsilyl groups using hexamethyldisilazane to determine the effects of the silanol groups on catalytic activity. The activities of the mesoporous silicas with or without capped silanols were compared to the activity of propylamine free in solution. Silylation resulted in a significant loss of activity, where turnover frequencies dropped nearly to those of the homogeneous base. The same behavior was also observed with dihydroimidazole-functionalized SBA-15, which catalyzes the Knoevenagel condensation by a different mechanism. Not only did these results indicate cooperative effects in heterogeneous systems, but cooperativity between a homogeneous base and silanols on unfunctionalized SBA-15 was also observed to a lesser extent. These results demonstrated that acid-base cooperativity seen in well-defined single sites can also be demonstrated on an extended catalytic domain on the surface of mesoporous silica where the active sites are not rigorously isolated.
Introduction

Many enzymes catalyze reactions by employing acid-base pairs within their active sites. Studies by Bass et al.\textsuperscript{1-3} copied this acid-base cooperativity by creating well-defined catalytic sites within silica, synthesized via an imprinting method.\textsuperscript{4} Using the Knoevenagel condensation reaction, they demonstrated acid-base cooperativity between silanol and aminopropyl groups within single sites. An important question is whether these isolated site results can be extended to catalysts with higher surface areas while maintaining the catalytic cooperativity. Additionally, to distinguish the role of the silanols as weak acids from the effect of the hydrophilicity or hydrophobicity of the catalyst surface, the effect of solvent on catalytic activity needs to be investigated. Another point of interest is whether the use of a different base that operates via a different mechanism will attain the same cooperative effects. The work described here examines the extension of the single site work performed by Bass et al. to functionalized mesoporous silica where co-condensed catalytic sites exist on extended surfaces.

The ability to achieve cooperative catalysis with functionalized mesoporous silica has recently been reported by Zeidan et al.\textsuperscript{5,6} in aldol condensation reactions. The cooperative effects were observed between sulfonic acid and thiol groups and sulfonic acid and amine groups. A recent study by Motokura et al.\textsuperscript{7} with amine-grafted amorphous silica-alumina used in three carbon-carbon bond forming reactions was similar to the study performed by Bass and coworkers. However, the support in the Motokura paper contained stronger Brönsted acids than the silica silanols and additionally included testing of homogeneous amines as well as mixtures of the unfunctionalized support and homogeneous amines. A limitation of that particular study was that it did not systematically investigate support-active
site cooperativity via the removal of the support component from an otherwise bifunctional system, which is addressed in the current work through silylation of the surface silanols. Additionally, the silica-alumina support lacked an ordered pore structure and the amines were grafted onto the surface, limiting the extension of these results to the design of a controlled catalytic domain in mesoporous silica.

Functionalization of mesoporous silica by co-condensation has the advantages of controllable loadings and more extensive distribution throughout pore surfaces over the alternative method, functionalization by grafting. Co-condensed mesoporous silica has extended pore wall surfaces that can serve as an uniform catalytic domain whereas silica gel can contain sites with limited accessibility due to their irregular pore structure. Additionally, amines that are grafted onto a catalyst are more vulnerable to leaching in aqueous solutions. Grafting tends to concentrate the groups around the exterior of the particle and tend to form “aminopropylsilane islands” while consuming multiple surface hydroxyl groups per grafted amine. Since co-condensation more uniformly incorporates functional silanes into the pore walls, more silanols generally remain available for catalytic activity.

Hexamethyldisilazane (HMDS) is commonly used to cap silanols and make silica surfaces hydrophobic. This reagent was used in the present study to observe the effects of the silanols on the catalyst’s activity. Chlorosilanes may also be used to silylate silica surfaces, but use of these requires a base catalyst. Silylation has been used to avoid inhibition of catalytic activity by surface silanols via hydrogen bonding and formation of zwitterions with primary amines, as well as competitive reactions.

The Knoevenagel condensation is a carbon-carbon bond-forming reaction commonly used to evaluate both organic and inorganic basic catalysts, so it was
used as the probe reaction. This reaction consists of the nucleophilic addition of a methylene group to a carbonyl group, where the methylene group is activated by one or two electron-withdrawing groups. Higher rates of reaction are obtained with aldehydes than with ketones due to steric and electronic effects.\textsuperscript{28,35}

In the current work, SBA-15 catalysts containing aminopropyl and dihydroimidazole groups were synthesized separately. Portions of each of these synthesized materials were then silylated with HMDS, so that the catalytic activities of all of these materials could be compared to one another as well as to that of a homogeneous base, propylamine.

**Experimental**

**Catalyst synthesis**

The aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) were synthesized using the co-condensation procedure described by Wang et al.\textsuperscript{30,45} In a typical synthesis, 4 g of the structure-directing agent, Pluronic P123 (BASF Co.) was dissolved in a mixture of 125 ml deionized water and 25 ml hydrochloric acid (12.1 N). Tetraethyl orthosilicate (TEOS, 98%, Acros Organics) was added as the silica precursor at 40°C. The functional silane, either 3-aminopropyltriethoxysilane (APTES) (99%, Aldrich) or N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (IPTES) (Gelest), was added after a TEOS prehydrolysis period of one hour. The resulting mixture (1 TEOS: 0.1 APTES/IPTES: 7.76 HCl: 171 H\textsubscript{2}O molar ratio) was stirred at 40°C for 20 h and aged at 90°C for 24 h before being filtered. The surfactant template was removed by refluxing in ethanol with 10 wt. % hydrochloric acid for 24 h. The catalyst was then filtered and washed with ethanol. Excess protons from the acidic synthesis conditions were removed with a 5 ml
tetramethylammonium hydroxide (TMAH) solution (25 wt. % in methanol, Acros Organics) in 45 ml methanol while stirring for 30 min.

**Silylation**

Following the TMAH treatment step, surface silanols were capped for a portion of the catalytic materials via silylation using an excess of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (ReagentPlus®, 99.9%, Aldrich). In order to avoid having traces of water in the pores during silylation, the catalysts were dried under vacuum at 100°C (20 µm Hg for 5 hours). 5 ml of HMDS was diluted in 5 ml toluene before addition to the suspension of the catalyst in toluene in a dry box. The mixture was refluxed for 24 h and was subsequently filtered and washed with toluene and ethanol. Figure 1 is a schematic of the sequential reaction of one molecule of HMDS with two silanols releasing ammonia and leaving the amine intact.

![Figure 1. Silylation reaction of aminopropyl-functionalized SBA-15 by HMDS.](image)

**Characterization**

Nitrogen adsorption/desorption was performed at -196°C with a Micromeritics ASAP 2020 system to obtain BET specific surface areas and BJH pore size distributions.
Thermogravimetric analysis (TGA) of silylated and unmodified aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) was performed with a Perkin-Elmer TGA7 for identification and quantification of functional groups using a temperature ramp of 5°C/min in a high purity nitrogen purge. The weight percent of nitrogen in each catalyst was determined by elemental analysis using a Perkin-Elmer Series II 2400 CHN analyzer. Fourier transform infrared spectroscopy (FTIR) transmission data were collected for pressed catalyst pellets made with potassium bromide using a Nicolet 6700 FT-IR (Thermo Electron Corp.).

**Catalytic testing**

Reactants for the Knoevenagel condensation reaction, benzaldehyde (ReagentPlus®, 99%+, Aldrich) and ethyl cyanoacetate (98%+, Aldrich), as well as propylamine (99%+), were used as purchased from Sigma-Aldrich. All reactions were performed in a 50-ml round-bottom flask agitated by magnetic stirring at 25°C with equimolar amounts of the reactants. The reaction was performed under a nitrogen blanket, which was added to purge the flask of air through one neck using a mineral oil bubbler. The catalyst was dried under vacuum at 100°C (20 µm Hg for 5 hours) prior to use. A typical reaction consisted of 0.14 g catalyst, 40 ml solvent (toluene or other as discussed later), 0.07 ml benzene as an internal standard, 0.91 ml benzaldehyde, and 0.96 ml ethyl cyanoacetate at 25°C. The reaction was initiated by addition of benzaldehyde to the reaction mixture. Samples were taken by syringe through a septum and analyzed using a Varian gas chromatograph (CP-3800) with a Varian CP7417 column and a flame ionization detector. As the condensation reaction of benzaldehyde with ethyl cyanoacetate is inhibited by the presence of water, the reactants were diluted in toluene and turnover numbers were calculated at moderate conversions to
minimize the concentration of water and, hence, equilibrium effects. The calculated turnover numbers were based on the conversion after 45 minutes of reaction time.

Results and Discussion

Characterization

For the silylated materials, the hydrophobicity of the catalyst was qualitatively apparent in its inability to be dispersed in water. Silylation was also confirmed by TGA, with a weight loss of about 10% of the total catalyst weight at around 400°C, which was consistent with the literature. As found previously with grafting, a nonpolar solvent allows aggregation of the silylation agent at the catalyst surface thereby favoring interaction with the silanols. Previously, the steric hindrance of the three methyl groups per silanol in HMDS resulted in incomplete surface coverage, which was found to be 82% by Anwander et al. However, it is believed that the long reaction times allowed for silylation facilitated capping all of the catalytically accessible silanols.

Nitrogen adsorption-desorption isotherms for the synthesized materials were of type IV with H1 hysteresis, characteristic of mesoporous solids with cylindrical pores. Physical properties of the materials are given in Table 1. The data for the silylated APS indicated a reduction in surface area and a slight reduction in pore size while maintaining the pore structure. The reduction in surface area upon silylation is consistent with previous reports. A comparison of the adsorption/desorption isothermals and pore size distributions for the APS and silylated APS samples is shown in Figure 2. The minor reduction in pore diameter implies that mass transfer within the pores of the unmodified and
silylated catalysts should be approximately equal, allowing the direct comparison of reaction data.

Table 1. Nitrogen adsorption/desorption and elemental analysis results for the heterogeneous base catalysts

<table>
<thead>
<tr>
<th></th>
<th>Surface area m²/g</th>
<th>Median pore diameter</th>
<th>Pore volume cm³/g</th>
<th>N content mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>570</td>
<td>52.4</td>
<td>0.75</td>
<td>1.05</td>
</tr>
<tr>
<td>Silylated APS</td>
<td>465</td>
<td>50.2</td>
<td>0.60</td>
<td>0.93</td>
</tr>
<tr>
<td>SBA-15</td>
<td>680</td>
<td>62.9</td>
<td>1.07</td>
<td>-</td>
</tr>
<tr>
<td>Silylated SBA-15</td>
<td>430</td>
<td>60.2</td>
<td>0.74</td>
<td>-</td>
</tr>
<tr>
<td>DHIS</td>
<td>610</td>
<td>60.3</td>
<td>0.88</td>
<td>1.01</td>
</tr>
<tr>
<td>Silylated DHIS</td>
<td>455</td>
<td>57.0</td>
<td>0.72</td>
<td>0.93</td>
</tr>
</tbody>
</table>

*From BJH adsorption

Figure 2. Nitrogen adsorption/desorption data for unmodified (■) and silylated (+) APS. (a) Nitrogen adsorption and desorption isotherms. (b) BJH adsorption pore size distribution.
FTIR spectra for the APS and silylated APS materials are shown in Figure 3. Incorporation of trimethylsilyl groups was confirmed by the Si-CH$_3$ antisymmetric deformation stretch at 1410 cm$^{-1}$. Both the silylated and unsilylated silicas display a large, broad silanol band in the region of 3700-3200 cm$^{-1}$. However, the silylated catalysts showed a significant decrease in the silanol bands. This result is mainly due to the conversion of silanols to trimethylsilyl groups, but the decrease is also likely due in part to diminished water adsorption from an increase in hydrophobicity. Free silanols have O-H stretching bands around 3740 cm$^{-1}$, while hydrogen-bonded silanols display stretching around 3600-3500 cm$^{-1}$. FTIR cannot distinguish between single and geminal silanols, as a result, peaks for the different silanols form a broad band. A Si-O-H stretching band can also be found in the region of 920-830 cm$^{-1}$. Large peaks protrude from the broad silanol band around 2970 cm$^{-1}$ in the silylated samples, corresponding to C-H stretching vibrations of the methyl groups. There is also a SiCH$_3$ band at 850 cm$^{-1}$. The significantly smaller adsorbed water peak around 1630 cm$^{-1}$ reveals the reduction in surface hydrophilicity.

**Reaction considerations**

Two mechanisms for the base-catalyzed Knoevenagel condensation have been proposed in the literature: a mechanism involving a covalent imine intermediate with the base group and an ion-pair mechanism. The presence of the imine intermediate for the former has been confirmed by *in situ* attenuated total reflection modulation infrared spectroscopy. Inorganic catalysts such as basic zeolites and higher order amines have been proposed to catalyze the reaction by the ion-pair mechanism. The ion-pair mechanism involves base abstraction of a proton from the methylene carbon, forming a
Figure 3. FTIR spectra of (a) aminopropyl-functionalized silica (APS) and (b) silylated APS.

carbon anion, which attacks the carbonyl carbon, forming an enol. The reaction concludes with
elimination of the hydroxyl group, forming a double bond and releasing water.\(^{40}\) When
uncatalyzed, the reaction proceeds through this mechanism in protic solvents.\(^{55}\) The reaction
order of the ion-pair pathway can be either first or second, depending on whether the proton
abstraction step or the condensation step is rate-limiting, respectively.\(^{41}\) The ion-pair
mechanism appears to be favored by tertiary amine groups, while primary amines, being
weaker bases, favor the imine intermediate.\(^{26,40}\) As a result of these different mechanisms for
different types of bases, the strength of the Brönsted base does not necessarily correlate with its catalytic activity.

Cooperative effects in the Knoevenagel condensation were first proposed by Hein et al.\textsuperscript{56} using a weakly basic ion-exchange resin, Dowex 3, in a mixture with acetic acid. The authors found that the acetate salt of Dowex 3 was more active than the resin alone but less active than the free basic form of the resin mixed with acetic acid. In the authors’ proposed mechanism, free acetic acid molecules activated the carbonyl while the basic resin moiety abstracted a proton from the methylene group. An equimolar combination of a weakly acidic (carboxylic acid) ion exchange resin and an aqueous base, \( \text{H}_2\text{N(CH}_2\text{)}_2\text{N}^+\text{Me}_3\text{ OH}^- \), has also been used as an acid-base catalyst system.\textsuperscript{57} The resin alone showed no catalytic activity. Use of a sulfonic acid resin, Amberlyst 15, with an amine was found to be ineffective in the condensation of benzaldehyde with ethyl cyanoacetate at room temperature due to the higher strength of the acidic moiety. The homogeneous equivalent of the amine and \( n \)-caproic acid also had little catalytic activity.\textsuperscript{57} Another cooperative interaction for the Knoevenagel condensation was reported by Kubota et al.,\textsuperscript{58} who found higher catalytic activities for organic cationic-MCM-41 composites than for the organic cations free in solution.

Acid-base bifunctional catalysis in the Knoevenagel condensation has been reported for inorganic catalysts via the ion-pair mechanism by Ebitani et al.\textsuperscript{39} using reconstructed hydrotalcite. The proposed mechanism began with the \( \text{Al}^{3+} \) cation acting as a Lewis acid site, coordinating with the nitrile group, thereby facilitating abstraction of the ethyl cyanoacetate proton and thereby stabilizing the resultant carbanion. Mild acid-base pairs in amorphous aluminophosphates and zirconophosphate oxynitrides have shown similar results, where acid-base pairs are more active than solitary bases of greater strength.\textsuperscript{37,42}
Angeletti et al. proposed adding participation of a neighboring silanol to the ion-pair mechanism in which the silanol forms a hydrogen bond with an aromatic aldehyde, thereby promoting nucleophilic addition of the anionic methylene compound.\textsuperscript{19} The participation of silanols in the reaction is also suggested by results of an infrared study by Corma et al.,\textsuperscript{23} where benzaldehyde was physisorbed onto substrates with different silanol densities, silica gel and MCM-41, with grafted “proton sponges,” 1,8-bis(dimethylaminonaphthalene). The authors found that the concentration of activated benzaldehyde was higher on MCM-41 than on silica gel, since the silica gel contained fewer silanol groups. This increase in activated benzaldehyde was found to correspond to higher catalytic activity in that study. However, it is possible that the role of the silanol in the condensation reaction is not merely hydrogen-bonding, but possibly transferring a proton. Such a role has been proposed in the literature for another cooperative system, a Henry reaction catalyzed by aminopropyl-functionalized silica gel.\textsuperscript{2} If this silanol proton transfer were also the case for the Knoevenagel condensation using the base-functionalized mesoporous silica described here, one could speculate the steps of a cooperative mechanism, as shown in Figure 4.
Figure 4. Postulated steps of the cooperative ion-pair mechanism. (A) The basic nitrogen abstracts a methylene proton, generating a carbanion. (B) The silanol protonates the benzaldehyde oxygen. (C) The carbanion reacts with the activated benzaldehyde. (D) Water and ethyl cyanocinnamate are formed and the catalyst returns to its initial state.

Similarly, cooperation between primary amine groups and silanols can also potentially aid in the formation of an imine intermediate. This possibility is suggested in a study by Hine et al., who demonstrated intra-molecular acid catalysis of the formation of imines from acetone and amines with hydroxyl groups. That study highlighted the ability of a hydroxyl group to protonate an amine in a bifunctional manner. A range of acid strengths have been reported for silanols, depending on the type of silanol and with some variation between studies, but these studies confirm that the pKₐ values of the silanols are below those of the bases used here, indicating their suitability for proton transfer. More recently, Bass
et al. proposed a cooperative acid-base mechanism for the imine intermediate pathway of a Henry reaction in their aminopropyl-functionalized silica gel. Correspondingly, the postulated steps of an acid-base cooperative mechanism for the Knoevenagel condensation reaction with a primary amine group are shown in Figure 5.

**Figure 5.** Postulated steps of the cooperative primary amine mechanism. (A) The silanol protonates the benzaldehyde oxygen while the amine undergoes nucleophilic attack on the carbonyl carbon. (B) Water is released in the formation of imine intermediate. (C) Ethyl cyanoacetate reacts with the intermediate. (D) Ethyl cyanocinnamate is formed and the amine is regenerated.
Catalytic testing

Shown in Table 2 are the Knoevenagel condensation reaction turnover numbers for the different catalysts systems performed at 25°C to minimize mass transfer effects. The turnover numbers were based on the number of sites per gram of catalyst as determined by elemental analysis. The aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) catalysts were active for the condensation reaction, with turnover numbers of 15.52 and 18.72 mol/site/hr, respectively, whereas the homogeneous propylamine showed little activity, with a turnover number of 0.66 mol/site/hr. Silylation of both catalysts resulted in a significant loss of activity, falling to 1.52 mol/site/hr for APS and 3.46 mol/site/hr for DHIS. The only minor reduction in pore diameter shown in the nitrogen adsorption/desorption results suggested that the rate suppression rate for the silylated APS for the condensation reaction was due to the lack of surface silanols rather than resistance to

Table 2. Knoevenagel condensation turnover numbers for homogeneous and heterogeneous base catalysts at 25°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Turnover number mol/site/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>Toluene</td>
<td>15.52 ± 1.24</td>
</tr>
<tr>
<td>Silylated APS</td>
<td>Toluene</td>
<td>1.52 ± 0.97</td>
</tr>
<tr>
<td>Propylamine</td>
<td>Toluene</td>
<td>0.66 ± 0.20</td>
</tr>
<tr>
<td>Propylamine + SBA-15</td>
<td>Toluene</td>
<td>3.78 ± 1.02</td>
</tr>
<tr>
<td>Propylamine + silylated SBA-15</td>
<td>Toluene</td>
<td>0.78 ± 0.26</td>
</tr>
<tr>
<td>DHIS</td>
<td>Toluene</td>
<td>18.72 ± 0.79</td>
</tr>
<tr>
<td>Silylated DHIS</td>
<td>Toluene</td>
<td>3.46 ± 0.92</td>
</tr>
<tr>
<td>DHIS</td>
<td>Acetonitrile</td>
<td>7.35 ± 0.81</td>
</tr>
<tr>
<td>Silylated DHIS</td>
<td>Acetonitrile</td>
<td>3.28 ± 0.36</td>
</tr>
<tr>
<td>DHIS</td>
<td>Methanol</td>
<td>22.39 ± 0.63</td>
</tr>
<tr>
<td>Silylated DHIS</td>
<td>Methanol</td>
<td>15.83 ± 0.79</td>
</tr>
</tbody>
</table>

Reaction conditions: 25°C, 40 mL toluene.
Errors represent 95% confidence intervals
internal mass transfer or blockage of amine sites. The silylated APS material turnover number was still greater than that for the homogeneous propylamine.

To determine whether the reaction needed silanol groups located in close proximity to the basic site, the activity of free propylamine in the presence of either unfunctionalized SBA-15 or silylated SBA-15 with co-condensed aminopropyl groups was tested. The conversion results for these tests are shown in Figure 6. Interestingly, the combination of unfunctionalized SBA-15 silica with free propylamine resulted in higher conversion than with the free propylamine alone, 21% versus 6% at 90 min, although the combination did

![Figure 6](image_url)

**Figure 6.** Conversion of ethyl cyanoacetate in toluene at 25°C. (○) homogeneous propylamine, (●) aminopropyl-functionalized SBA-15 (APS), (■) mixture of propylamine and unfunctionalized SBA-15, (★) silylated APS, (▲) mixture of propylamine and silylated, unfunctionalized SBA-15.
give lower conversion than the co-condensed aminopropyl-functionalized silica, 32% at 90 min. It is possible that propylamine may form the imine intermediate while free in solution before diffusing near the silanols. As demonstrated by the comparative rates, the location of the tethered basic site in close proximity to silanols gave a significantly higher rate of reaction. This behavior has also been reported in the literature by Kubota et al., who demonstrated higher catalytic activities for FSM-16–supported secondary amines than those for homogeneous secondary amines mixed with FSM-16 in an aldol reaction.\textsuperscript{63}

The dihydroimidazole-functionalized silica is a stronger base than the primary amine-functionalized silica, but is unable to form the imine intermediate and must proceed through the carbanion intermediate. The reaction rate for this amine was also aided by having surface silanols in close proximity as shown by the conversion results in Figure 7, where silylation decreased the conversion at 90 min from 36% to 7%. This catalyst, with a moiety that is a stronger base than propylamine, displayed slightly higher activity than the APS catalyst. Despite having different underlying mechanisms, silylation of the DHIS catalyst had similar results to that of the APS catalyst, showing a significant reduction in activity. Silylation of the DHIS possibly reduces activity in two ways: a loss of silanols to

Comparison of the conversion results provided some additional information about the reaction system. Unfunctionalized SBA-15 alone displayed no catalytic activity, which was consistent with the literature.\textsuperscript{64} A mixture of silylated APS particles with unmodified SBA-15 silica particles showed approximately the same catalytic activity as the silylated APS, demonstrating that the silanols and amine moieties must be in proximity in order to attain significantly higher reaction rates. Additionally, this result indicates that the contribution from the silica support was due to the participation of the silanols rather than the adsorption
Figure 7. Conversion of ethyl cyanoacetate at 25°C in toluene with (●) dihydroimidazole-functionalized SBA-15, (DHIS), (■) silylated DHIS.

of water onto the silica surface, which would remove water produced by the condensation reaction from solution. Incomplete silylation of the silanols could account for the slight increase in turnover number for the propylamine in solution with silylated SBA-15 over the free propylamine alone. Previous studies have shown that the steric bulk of the three methyl groups as well as hydrogen-bonding of silanols prevents complete silylation by HMDS. However, it is likely that HMDS reacted with nearly all of the accessible, reactive silanols. Another possible explanation is that, although much care was taken to wash the catalyst after silylation and to dry the catalyst using heat and strong vacuum, there could have been some traces of ammonia left adsorbed on the surface of the catalyst that could have contributed to the reaction rate. The nearly identical activities of the homogeneous propylamine and the
propylamine in solution with silylated, unfunctionalized SBA-15 indicate that this is likely to be minor;

**Apparent activation energies**

Apparent activation energies were calculated from initial rates data obtained at 25°, 35° and 45°C in toluene (the boiling point of propylamine is 48°C). Using an overall second-order rate law that was first order with respect to ethyl cyanoacetate and benzaldehyde, which had a linear fit with an R² value greater than 0.99, apparent activation energies of 25.3 kJ/mol for the homogeneous propylamine and 61.2 kJ/mol for the APS catalyst were determined. Calculating apparent activation energies using a first order (ethyl cyanoacetate only) rate law resulted in a slightly poorer fit but similar numbers, similar to a study with the same reactants but different catalysts, alkaline-substituted sepiolites. Pre-exponential factors of 0.42 and 18 L/mol/s were calculated for the homogeneous and heterogeneous catalysts, respectively. The result for the combination of unfunctionalized SBA-15 and homogeneous propylamine gave an intermediate value of 32.1 kJ/mol with a pre-exponential factor of 5.1 L/mol/s. Interestingly, the more active heterogeneous catalyst was found to have a lower activation energy than the less effective homogeneous catalyst.

Reports of activation energies in the literature for the same reactants indicate that the values found in the current work are consistent. For homogeneous catalysts operating via the ion-pair mechanism, activation energies for the condensation of benzaldehyde and ethyl cyanoacetate reported in the literature range from 21 to 37 kJ/mol (5 to 8.8 kcal/mol). Whereas, for some alkaline-substituted sepiolites (Li, Na, K, Cs on magnesium silicate), which also form the carbanion intermediate, activation energies from 32 to 72 kJ/mol have been reported for the same reactants in the absence of a solvent. That study was a
continuation of work using zeolites as the support for the same alkali metal cations in which the authors compared the activity of their heterogeneous catalyst to homogeneous pyridine. Pyridine was found to have an intermediate activity between X and Y zeolites, where X zeolites are more basic and more active, as well having an intermediate activation energy of 44.3 kJ/mol. Interestingly, pyridine was less active than all but one of the sepiolite catalysts, yet its activation energy was lower than those for the lithium and sodium catalysts and higher than those for the potassium and cesium catalysts.

The trend in the pre-exponential factors appeared reasonable, since the reactants encountering amine sites incorporated in the mesoporous silica would also be in proximity to one or more silanols, making the site better positioned for catalysis than the homogeneous amine by itself. When dispersed with unfunctionalized silica, the homogeneous amine could diffuse through the solvent and interact with reactants at the silica surface. Since the amine groups in this case were not fixed to the surface, a lower probability of successful alignment of the reactants with the catalyst would be expected.

**Solvent effects**

To better discern the effects of silylation on catalytic activity, the DHIS and silylated DHIS catalysts were also tested using either methanol or acetonitrile as the solvent. These experiments were necessary because silylation turns a hydrophilic silica surface into a hydrophobic surface, which would affect the interactions between the reagents and the catalytic sites. The difference between the imine intermediate and ion-pair mechanisms was apparent in opposing solvent trends reported in the literature. Activity of catalysts using the ion-pair mechanism increased in solvents with increasing polarity, while the opposite was true for heterogeneous primary amine catalysts. Nonpolar solvents appeared to aid
the primary amine mechanism by concentrating the reactants at the catalyst surface.\textsuperscript{21} Al-Haq et al.\textsuperscript{33} demonstrated an opposite trend with aminoalkyl modified polysilsesquioxanes, where catalytic activity increased with increasing solvent polarity. These results appeared to support the hypothesized partitioning effect since the polysilsesquioxanes are more hydrophobic than silica materials synthesized using tetraethoxysilane or tetramethoxysilane, and consequently, would not concentrate polar reactants near the catalyst surface. This suggests that the activity of the combination of unfunctionalized SBA-15 and homogeneous propylamine may be aided in part by some partitioning of the propylamine near the hydrophilic surface. Polar solvents aid the ion-pair mechanism by stabilizing the carbanion intermediate, as shown by observed activation energies in various solvents by Rodriguez and Corma et al.\textsuperscript{29} using an unsupported organic “proton sponge” catalyst. This study reported activation energies of 5 kcal/mol when dimethyl sulfoxide was the solvent, 8.5 kcal/mol for chlorobenzene and 7.7.3 kcal/mol for no solvent. Corma et al.\textsuperscript{23} found that having sufficient silanols on the silica surface appeared to stabilize the transition state, thereby reducing the effect of the solvent on catalytic activity. Despite the inhibition of condensation reactions by water, the Knoevenagel condensation reaction was shown to proceed in aqueous solution presumably due to stabilization of the ion-pair intermediate.\textsuperscript{24}

The activity results for the DHIS functionalized silica catalysts in different solvents are shown in Table 2. When acetonitrile (dielectric constant, $\varepsilon_r = 37.5$ \textsuperscript{67}) was used as the solvent, the condensation reaction catalyzed by DHIS was significantly slower than that obtained in either toluene or methanol probably due to the solvent’s inability to stabilize the carbanionic intermediate.\textsuperscript{67} The activity of the silylated catalyst was slightly lower in acetonitrile than in toluene. This indicates that the polar capping agent used by Bass et al.,
dimethyl cyanopropyl chlorosilane, is not ideal for a study of this catalyst and highlights the need for catalytic testing in a solvent that can stabilize the intermediate in order to distinguish between noncovalent interactions and acid-base cooperativity.\(^2\)

The condensation of ethyl cyanoacetate and benzaldehyde in methanol \((\varepsilon_r = 32.6\) \(^67\)) was complicated by base-catalyzed transesterification of ethyl cyanoacetate and ethyl cyanocinnamate into methyl cyanoacetate and methyl cyanocinnamate, respectively.\(^{38}\) Interestingly, the transesterification reaction in methanol without benzaldehyde was negligible when the silylated DHIS catalyst was used. However, despite the added complexity of the tranesterification side reaction with methanol as the solvent, conclusions may still be drawn from the conversion of benzaldehyde as well as from the combined conversion of the two alkyl cyanoacetates even in the presence of methanol. The catalyst displayed higher activity in methanol than in toluene, which is consistent with other organic catalytic groups supported on silica that operate via the ion-pair mechanism.\(^{23}\) Although there was a slight decrease in activity for silylated DHIS, the effect of silylation was not nearly as dramatic in methanol as that seen in toluene. As the influence of solvent on activity became less significant when polar, protic solvents were used, as shown in the literature.\(^{23}\) Similarly, that current results show that methanol, a protic solvent, appears to stabilize the carbanion intermediate, thereby reducing the effect of the silanols. It is important to note that this observation does not conflict with the proposition of the silanol acting cooperatively as an acid in the Knoevenagel condensation reaction. The activity difference between the DHIS and silylated DHIS catalysts in general was much greater than the activity difference between the DHIS catalyst in toluene and in methanol. This result supports that hypothesis the silanols do not merely hydrogen bond with the reactants. Additionally, the small decrease in activity
of the silylated DHIS in methanol and the relative ease of the transesterification reaction indicated that the large decrease in activity with toluene as the solvent was not due to mass transfer effects or steric hindrance of the trimethylsilyl groups.

**Conclusions**

Random incorporation of amines via co-condensation of SBA-15 was found to yield acid-base cooperative catalysis with surface silanol groups. While cooperative activity was achieved with a solution containing a mixture of propylamine and SBA-15, the activity increased significantly when the aminopropyl groups were attached near silanol groups. Thus, previous single-site results can in some cases be extended to a more extended catalytic domain where the active sites are not rigorously isolated as in functionalized mesoporous silica. Additionally, this study has shown that the dihydroimidazole moiety, which catalyzes the Knoevenagel condensation via an ion-pair mechanism, also displays acid-base cooperative behavior. While solvent effects were significant, the presence of silanols was shown to have a greater impact on catalytic activity. These results support the hypothesis that the silanols act as acids rather than merely stabilizing transition states with hydrogen bonds. While solvent effects were significant, the presence of silanols was shown to have a greater impact on catalytic activity. Consideration of these results can be of use when designing a co-condensed acid-base bifunctional catalyst, where the proximity of the acid and base groups determines catalytic activity and reaction selectivity. Additionally, the silylation experiments performed here may also be of use when testing a new acid-base catalyst in order to elucidate the catalytic mechanism of the organic moiety from the effects of silanol groups.
Acknowledgments

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References

(18) Knoevenagel, E. Berichte der Deutschen Chemischen Gesellschaft 1898, 31, 738-748.


Appendix A. Temperature-dependent catalytic data

Figure A.1. Conversion of ethyl cyanoacetate catalyzed by propylamine in toluene: (○) 25°C, (+) 35°C, (∗) 45°C.
Figure A.2. Conversion of ethyl cyanoacetate catalyzed by propylamine and unfunctionalized SBA-15 in toluene: (○) 25°C, (+) 35°C, (×) 45°C.
Figure A.3. Conversion of ethyl cyanoacetate catalyzed by aminopropyl-functionalized SBA-15 in toluene: (○) 25°C, (+) 35°C, (×) 45°C.
Chapter 4. The Hydrocarbon Pool in Alcohol-to-Gasoline over H-ZSM-5 Catalysts

Abstract

The methanol-to-gasoline (MTG) process is gaining increased interest as a route to liquid fuel from natural gas, coal, or gasified biomass. This process was first developed in the 1970s by the Mobil Research and Development Corporation. It is catalyzed by acidic zeolites, initially H-ZSM-5, and produces a variety of hydrocarbons: olefins, paraffins, aromatics, and other nonaromatic hydrocarbons. Consequently, other names have been used for this reaction system depending on the products of interest, such as methanol-to-hydrocarbons (MTH) and methanol-to-olefins (MTO). The goal of this work was to investigate the hydrocarbon pool mechanism within the zeolite used in this process via analysis of material retained in the pores when alternative alcohols are used as feeds. An improved understanding of the pore environment and the reaction mechanism is essential for designing a catalyst for a particular selectivity. This chapter covers work done with this reaction at the Center for Sustainable and Green Chemistry (CSG) at the Technical University of Denmark, Lyngby in the summer of 2008 through the Partnerships for International Research and Education (PIRE) program funded by the National Science Foundation. This PIRE program is entitled: Molecular Engineering for the Conversion of Biomass Derived Reactants to Fuels, Chemicals, and Materials. This chapter includes results that will be published in Catalysis Letters and are currently available online.
Introduction

Mobil developed the methanol-to-gasoline process in the 1970s and 80s and commercialized the process in New Zealand using natural gas as the feedstock. Starting in 1986, 600,000 tons of gasoline were produced annually at Mobil’s Motunui methanol plant. However, the MTG process was discontinued in the 1990s due to the low cost of gasoline from crude oil relative to the price of methanol. Now that the cost of crude oil is increasing and the production of methanol is on the rise, the MTG process is currently regaining favor as an attractive alternative route to gasoline. The plant in New Zealand has been reopened by Methanex Corporation in 2008 for the annual production of 900,000 tons of gasoline.

Today, as interest in the MTG process grows, other feeds are being considered as alternatives or as complements to the methanol feed. For example, a variety of alcohols can be produced from syngas following the gasification of biomass and then fed to a gasoline production process. Additionally, partially distilled bio-ethanol has also become a feed of interest, since catalyst deactivation from coking has been shown to be inhibited by addition of water to the feed. Use of this feed would add additional water to the reaction, thereby inhibiting catalyst deactivation while reducing the costly extent of distillation required. Ethanol-to-gasoline (ETG) has been the subject of several studies and has been shown to produce the same products as MTG. Since MTG and ETG result in the same products, these reactions likely proceed through similar routes. However, while there are some plausible theories, the reaction mechanism is not completely understood. The current theory is known as the hydrocarbon pool mechanism, which has been developed with the aid of experimental data regarding the compounds within the pores of the zeolites used as catalysts for this reaction. The goal of this work is to gain a better understanding of the reaction.
mechanism in the alcohols-to-gasoline process by examining the composition of the hydrocarbon pool retained within the zeolite H-ZSM-5. Different alcohols and mixtures of alcohols were used as feeds with the same process conditions for comparison of the materials retained within the catalysts. The contents of the hydrocarbon pool within the zeolite pores have not been reported in the literature for ETG or for other alcohols to gasoline. The results of this study aim to advance the understanding of the general mechanism for alcohols-to-gasoline and consequently the MTG mechanism because of the similarities between the processes.

**Background**

The catalysts used in the MTG process are zeolites, initially H-ZSM-5, but other types such as H-beta and H-SAPO-34 have also been studied. Zeolites are porous crystalline aluminosilicate materials with an entirely tetrahedral framework. This framework has been defined as four oxygen atoms surrounding a cation. The chemical formula of a zeolite can be expressed as:

\[
A^{m+}_{\delta/m} \left[ (\text{SiO}_2)_x \cdot (\text{AlO}_2^-)_y \right] \cdot z\text{H}_2\text{O}
\]

where A is a cation with the charge m, \((x+y)\) is the number of tetrahedral per crystallographic unit cell, and \(x/y\) is the Si/Al ratio. These materials have porosity in the form of channels and cages. H-ZSM-5, a common MTG catalyst, shown in Figure 1 is an acidic aluminosilicate with a system of 10-ring channels in two dimensions. This ring structure is shown in Figure 1a and the pore structure is shown in Figure 1b. The pores in this zeolite have the dimensions: 5.4 × 5.6 Å. The cages of the zeolite are formed by the intersection of
the channels shown in Figure 1b. H-beta has larger pores: $7.6 \times 6.4 \, \text Å$.\textsuperscript{19} H-SAPO-34 has $7 \times 10 \, \text Å$ cages connected by $3.8 \times 3.8 \, \text Å$ channels.\textsuperscript{19}

![Figure 1](image1.png)

**Figure 1.** a) Zeolite ZSM-5 molecular structure,\textsuperscript{20} b.) ZSM-5 pore structure.\textsuperscript{21}

**Reaction mechanism**

The MTG process has been studied extensively since its inception. The basic premise in the literature for the mechanism for the production of hydrocarbons within zeolites is the hydrocarbon pool model proposed by Dahl and Kolboe in 1993.\textsuperscript{22} The MTG reaction begins
with the rapid two-step dehydration of methanol to dimethyl ether.\textsuperscript{23} After further dehydration, toluene is formed, which is easily methylated into xylenes and other higher methyl benzenes.\textsuperscript{24,25} The hydrocarbon pool mechanism, which has been developed over the past 15 years, suggests that the actual catalytic sites in the zeolite are organic-inorganic hybrids consisting of cyclic organic species trapped within the zeolitic framework, particularly polymethyl benzenes.\textsuperscript{18,22,24,26-31} These organic species act as the hydrocarbon pool from which the products in the exit gas stem via cracking. The MTG process has been extensively studied by Kolboe et al., who studied the nature and amount of retained material within H-beta,\textsuperscript{26,32,33} SAPO-34,\textsuperscript{27,34} and H-ZSM-5\textsuperscript{24,35} catalysts. These authors gained considerable insight into the mechanism by determination of material retained within the used catalyst and many aspects of the hydrocarbon pool model stem from their work. Although the concept of the hydrocarbon pool has been widely accepted, the exact mechanism following the formation of alkylated aromatics has been debated in the literature. Two main reaction mechanisms for the hydrocarbon pool have been proposed: an exocyclic methylation reaction\textsuperscript{36-38} and a paring reaction.\textsuperscript{26,38,39} The exocyclic methylation mechanism was proposed by Mole et al.\textsuperscript{36,37} and is shown in Figure 2.\textsuperscript{39} This pathway begins with the heptamethyl benzenium ion, heptaMB\textsuperscript{+}, which is formed when hexamethyl benzene receives a CH\textsubscript{3}\textsuperscript{+} ion and may be found in equilibrium with the deprotonated form, 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (HMMC).\textsuperscript{39,40} The exocyclic double bond of HMMC can react with methanol, resulting in an ethyl group that is then split off as ethylene.\textsuperscript{39} Similarly, propylene can be produced if the ethyl group is instead deprotonated and subsequently methylated. After the alkene has been split off, a proton is returned to the
zeolite, producing hexamethyl benzene. In the alternative pathway proposed in the literature, the paring mechanism, an aromatic ring undergoes expansion and contraction,

![Figure 2. Exocyclic methylation mechanism.](image)

whereby an alkyl side chain grows, as shown in Figure 3. After ethylene or propylene is split off from the ring, whereupon hexamethyl benzene is regenerated by subsequent ring methylation. This is in contrast to the exocyclic mechanism, where the side chain is directly alkylated, not the ring. Support for the paring mechanism has come from isotopic studies that indicate “scrambling” of $^{13}$C from $^{13}$C-methanol with $^{12}$C-benzene in the rings of resulting methyl benzenes. More recently, Cui et al. reported hydrogen/deuterium exchange on toluene even when no olefins were produced. The authors determined that the deuterated methanol would exchange its methyl group with a toluene molecule and subsequently undergo ring contraction followed by ring expansion accompanied by a proton/hydride transfer between the methyl group and a ring carbon, in agreement with the
paring mechanism.\textsuperscript{44} However, a theoretical study by Arstad et al.\textsuperscript{42} using density functional theory favored the exocyclic mechanism over the paring mechanism.

\textbf{Figure 3.} Pairing mechanism.\textsuperscript{39}

There are some differences in the behavior within the hydrocarbon pool between different zeolites. In a study of various zeolites, Cui et al.\textsuperscript{43} reported that the reaction occurs only on zeolites that facilitate the hydrocarbon pool mechanism. For example, the 5.7 Å pores of ZSM-22 are not large enough to accommodate the active aromatic intermediates of MTG (only a small amount of xylene was detected in the pores), and consequently was unable to convert methanol into olefins, even in the presence of toluene.\textsuperscript{43} However, the channels of H-ZSM-5 are wide enough to allow the internal generation of polyalkyl benzenes as well as the passage of some alkylated benzene rings. When either H-beta or H-SAPO-34 is used, the most reactive molecule found in the retained material is hexamethyl benzene, consistent with the pathways in Figures 2 and 3.\textsuperscript{27,35} However, this has been shown to not be
the case when H-ZSM-5 is used; conversely, penta- and hexamethyl benzene were found by Bjørgen et al.\textsuperscript{24,35} to be “virtually unreactive” in studies where \textsuperscript{13}C methanol was fed to the process following \textsuperscript{12}C methanol. Furthermore, Bjørgen et al. claimed that the channels of H-ZSM-5 are not wide enough to facilitate the methylation of hexamethyl benzene that forms heptaMB+, so a different mechanism must be at work in H-ZSM-5.\textsuperscript{24} Bjørgen et al. also reported that while ethylene appeared to be formed from xylenes and trimethyl benzenes, higher alkenes, particularly propylene, are produced by a different cycle that is not based on aromatic compounds.\textsuperscript{42,45} Consequently, there appear to be two simultaneous, connected pathways within the hydrocarbon pool in H-ZSM-5: one cycle generates ethylene and aromatics while another produces propylene and higher alkenes, as proposed by Bjørgen et al.\textsuperscript{24} in 2007. Computational work has indicated that ethylene cannot be formed directly from methanol.\textsuperscript{23} A schematic from that paper showing the Bjørgen et al.’s proposed dual cycle

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{The dual cycle mechanism proposed by Bjørgen et al., b) Alkene cracking/methylation route to propylene proposed by Bjørgen et al.\textsuperscript{24}}
\end{figure}
mechanism is shown in Figure 4a. Figure 4b shows the authors’ proposed alkene cracking/methylation route to propylene, where methyl groups from methanol are added sequentially to propylene to form hexene, which splits into two molecules of propylene. These two cycles are not believed to be completely independent; some higher alkenes produced by Cycle II are likely to undergo aromatization and enter Cycle I due to the continuous production of aromatics observed.

In a recent paper, McCann et al. proposed a catalytic cycle based on the paring mechanism, citing support from experimental and computational studies, shown in Figure 5. This cycle begins with toluene, as does Bjørgen et al.’s Cycle I, which in this case undergoes successive methylations to form tetramethyl benzene, then a pentamethyl benzenium cation. The cation undergoes intramolecular isomerizations and a ring contraction, and then splits off.

![Figure 5. Catalytic cycle producing isobutene, adapted from McCann et al.](image-url)
isobutene. A ring expansion step transforms the cation back into toluene. This mechanism does not include hexamethyl benzene or heptaMB+ and accounts for the production of isobutene from methanol. However, Bjørgen et al.\textsuperscript{24,46} argue that isotopic studies indicate that ethylene and C\textsubscript{8}-C\textsubscript{10} aromatics come from the same cycle, whereas C\textsubscript{3}-C\textsubscript{6} alkenes come from a separate pathway, contradictory to the aromatic-based pathway to isobutene proposed by McCann et al. Evidently, more studies of the hydrocarbon pool are needed to understand the alcohols-to-gasoline pathway.

**Experimental**

**Atmospheric pressure setup**

The catalyst used in this study was H-ZSM-5 (Si/Al = 11.5, 40), supplied by Zeolyst International. This zeolite was fractionated and sieved to particles in the range of 300 μm to 710 μm. Initial experiments were performed in a continuous flow fixed bed quartz tubular reactor with an inner diameter of 6 mm. Figure 6 is a schematic of the reactor system. The temperature of the catalyst bed was maintained at 450°C in an oven, with a thermocouple situated immediately below the catalyst bed. The ethanol/water mixtures were added through a HPLC pump, evaporated by heating tapes and carried through the catalyst bed with a flow of helium at 40 ml/min. The product distribution of the exit stream was analyzed using an Agilent 6890 GC equipped with a Varian PoraPlot Q-HT column and a flame ionization detector (FID). This system was set up for automatic sampling every hour of the product gases. The weight hourly space velocity (WHSV) for this setup was 9 h\textsuperscript{-1}. This setup also allows the preheated feed to bypass the reactor prior to the start of the reaction. At the end of
a run, the reactor was immediately moved to another oven where the catalyst was flushed with helium for 5 minutes at 55°C.

![Flow reactor system](image)

**Figure 6.** Flow reactor system.⁴⁷

**High pressure setup**

The experiments comparing ethanol feeds with methanol and other alcohol feeds were performed on a similar setup with a stainless steel reactor. The alcohol/water mixture was fed into the top of the reactor within the oven where the feed was allowed to vaporize on quartz wool between the reactor inlet and catalyst bed. This system includes a condenser to separate gaseous products from condensable products before the gaseous products of the stream are analyzed on an Agilent 6890 GC equipped with a J&W Scientific GS-Gaspro column and a FID. Automatic sampling every hour was used for the exit gases. Experiments were carried out at 400°C with a WHSV of 6 h⁻¹. When higher alcohols, mixtures of alcohols
and acetone were fed to this process, water was used as diluent to keep the number of moles of carbon per time constant.

**Analysis of retained material**

Determination of the composition of the hydrocarbon pool utilized the zeolite dissolution method of Guisnet et al.\textsuperscript{48,49} 100 mg of spent catalyst was dissolved in 3 ml of 20\% wt. hydrofluoric acid in a closed Teflon vial. The mixture was shaken and allowed to stand overnight. When the zeolite was dissolved, the retained material was extracted with 1 ml of dichloromethane with added chlorobenzene as an internal standard. The organic phase was filtered and most of the dichloromethane was allowed to evaporate. The concentrated samples were then analyzed on an Agilent 6850 GC with a quadruple mass spectrometer detector 5975C.

**Results and Discussion**

**Methanol- and ethanol-to-gasoline**

The major gaseous products of the ETG process are the same as the products of the MTG process, as shown in Figure 7 after two hours on stream at 400°C and 10 bar. This is consistent with reports on ETG in the literature.\textsuperscript{10-15,50} Although the proportions of the gases produced vary with time as the catalyst deactivates, the most abundant gases present in both exit streams prior to deactivation are propane and butanes. Only a small amount of methane is produced.

The liquid products of the two processes are also similar. The gas chromatography results in Figure 8 show the condensable components of the exit stream after two hours at
Figure 7. Gaseous products from reaction over H-ZSM-5 at 450°C and 1 bar.\(^3\)

Figure 8. Liquid products from reaction over H-ZSM-5 at 450°C and 1 bar as analyzed using gas chromatography\(^3\)
400°C and 10 bar. This figure shows that the major products of both feeds include benzene, toluene and xylenes. However, the condensables in the exit streams are seen to have some differences in their content of higher aromatics when analyzed using mass spectrometry, as shown in the total ion chromatograms in Figure 9. The ETG process creates more aromatics with ethyl substituents than does the MTG process. These results are not surprising, as ethanol would be expected to ethylate the aromatics in the hydrocarbon pool in a similar manner as that of methanol methylation. The most significant difference between the ETG and MTG liquid product composition is that tetramethyl benzene is present in the methanol process liquid products and absent in the ethanol process liquid products. Conversely, dimethyl ethyl benzene is found in the ETG condensate but not in the MTG condensate. Additionally, while methyl ethyl benzene is much more significant than trimethyl benzene in ETG, the reverse is true for MTG.

Due to the similarities between the reactor effluent of both processes, one would expect the catalyst to operate by the same general reaction mechanism. However, it is likely that the reactor effluent components differing between MTG and ETG are generated from corresponding compounds within the hydrocarbon pool. Consequently, the used zeolites were dissolved to facilitate analysis of the hydrocarbon pool. The concentration of the organic material following extraction from the zeolite has been shown by Arstad et al. to not have an effect on the composition of the extracted sample. The most significant compounds released from the zeolites for MTG and ETG are shown in Figure 10. Some of these compounds were also found in the condensable fraction of the reactor effluent, such as xylenes and trimethyl benzene, which remained adsorbed on the zeolite after flushing the catalyst bed with helium. However, tetraethyl benzene, triethyl methylbenzene, triethyl
benzene, diethyl dimethyl benzene and diethyl methyl benzene were found in the ETG retained material but not in the reactor effluent. The lower methyl benzenes were common to both processes, but the highest methyl benzenes, tetramethyl benzene, pentamethyl benzene
and hexamethyl benzene were only found in MTG. Conversely, the higher ethyl and mixed methyl ethyl benzenes found exclusively in the retained material were only found in the ETG process. Although there are these differences between MTG and ETG involving the higher polymethylbenzenes and other substituted benzenes, it is not surprising that many of the products are the same for the two processes. The commonality of the lower substituted benzenes in the retained material along with the gaseous products and most of the liquid products are consistent with Bjørgen et al.’s postulated dual cycle, where Cycle I, involving trimethylbenzene and toluene, generates ethylene and aromatic compounds. However, it is unclear how the higher ethyl benzenes and mixed methyl ethyl benzenes fit into the mechanisms proposed in the literature.

**Time studies**

The next experiments sought to determine how the composition of the hydrocarbon pool of the ETG process in H-ZSM-5 changes with time, which may indicate the reactivities
of different retained methyl and ethyl benzenes. At the end of a run, the catalyst bed was flushed with helium to remove small molecules not trapped inside the zeolite pores as well as any larger molecules on the exterior of the zeolites. Heated flushing experiments were also performed, where helium flowed through the catalyst bed at reaction temperature. Results from GC-MS for used zeolites after 15, 60 and 120 minutes on-stream at 450°C and 1 bar are shown in Figure 11. In this figure, it can be seen that the amount of tetraethyl benzene and triethyl methyl benzene retained in the zeolite increased with time on-stream while the amount of methyl benzenes remained roughly the same. This implies that the methyl benzenes are more reactive than the higher ethyl benzenes, as they likely react about as quickly as they form after an initial induction period. Conversely, tetraethyl benzene and triethyl methyl benzene appear to have minimal reactivity, as the amounts of these compounds build over time to become the dominant species present in the hydrocarbon pool after 120 minutes on-stream. These two components of the hydrocarbon pool could be considered “dead ends” for the ETG reaction in the same manner as pentamethyl benzene and hexamethyl benzene in the MTG reaction, as found by Bjørgen et al.\textsuperscript{24} To better understand how these species behave in the hydrocarbon pool, a run was repeated where the catalyst was flushed with helium at reaction temperature. It was hypothesized that if tetraethyl benzene and triethyl methyl benzene were dead ends, then these compounds would persist within the pores of the catalyst throughout hot flushing. However, the amounts of these two species decreased significantly. There are two possible explanations for this behavior; either these two species go on to form coke deposits or they are a less reactive component of the pool and crack into smaller molecules. In either case, neither of these species is likely to have a significant effect on the overall product distribution.
Figure 11. Total ion chromatographs of ETG retained material after on-stream times of a) 30 min, b) 60 min, and c) 120 min.³

Deactivation

Since H-ZSM-5 has smaller channels than some other MTG zeolites, it is believed that pore size restriction limits the development of polycyclic aromatics that lead to coke formation, giving it greater resistance to deactivation than other zeolites.⁴⁹,⁵¹ Consequently, the main deactivation route for H-ZSM-5 is reported to be external coking.²⁴,⁵²,⁵³ Coking was apparent for every catalyst sample used, regardless of the type of alcohol fed to the process. The H-ZSM-5 catalyst was initially white and turned gray to black, depending on time on-
stream; even the sample used for only 15 minutes became gray. The larger alkylated benzenes such as tetraethyl benzene and triethyl methyl benzene could progress to naphthalenes and other coke precursors, which were found in the retained material after longer reaction times. In this study, two types of H-ZSM-5 were used, with Si/Al ratios of 11.5 and 40. The change to a zeolite with a Si/Al ratio of 40 was made due to the rapidity of coke formation at a ratio of 11.5. This difference is due to the acidity of the zeolites, since deactivation occurs more quickly on zeolites with higher acid site densities. The acidity of the zeolite depends on the silica/alumina ratio, where the acid site density is inversely proportional to the Si/Al ratio. Deposition of coke also strongly favors acidic sites. Zeolite coking has multiple effects: reducing the acidity of the catalyst by adsorption on acid sites and blocking pores. In the MTG process, deactivation was seen as a decline in all products and an increase in dimethyl ether. The amounts of ethylene and propylene increased

Figure 12. Light olefins and paraffins produced from methanol at 400°C, 10 bar.
to a maximum before decreasing. These changes over time are shown in Figure 12. Similarly, in the ETG process, deactivation was seen as an increase in the amount of ethylene produced along with a decline in all other products. As the catalyst deactivated, the amount of propane produced decreased, while the amount of propylene produced gradually increased over time to a maximum, and then gradually decreased. These changes in the gaseous products are shown for ETG in Figures 13 and 14. This is consistent with the literature, where the formation of ethylene and the ratio of ethylene to propylene have been shown in the literature to be enhanced by coking. When ethanol was used, the catalyst appeared to deactivate more quickly than when methanol was the feed. Ethanol is rapidly dehydrated into ethylene, which readily forms coke on H-ZSM-5. However, a comparison

Figure 13. Light olefins and paraffins produced from ETG at 400°C, 10 bar.
Figure 14. Composition of gaseous product stream from ETG at 400°C, 10 bar.

of deactivation by the two alcohol feeds is complicated by the difference in carbon content. When the same water volume fraction was used for the ethanol and methanol feeds, the number of moles of carbon was significantly higher for ethanol. Consequently, in order to compare the two alcohols at the same carbon molar feed rate, water was used as a diluent. As a result of the higher water content in the ethanol feed, the catalyst used for ETG deactivated more slowly than that used for MTG. The effect of water is either to displace coke on the zeolite surface or to promote coke cracking reactions. Different proportions of water in the ethanol feed did not affect the composition of the reactor effluent. Water is not believed to cause significant dealumination in these experiments, since Aguayo et al. found the limiting conditions for reversible deactivation to be 450°C and a water content of 50%.
Other feeds and mixtures

For a better understanding of this reaction system, a variety of feeds were tested: some higher alcohols, mixtures of alcohols and acetone, all containing water. Whereas ethanol and methanol are primary alcohols, the compositions of the hydrocarbon pools resulting from secondary and tertiary alcohols were additional points of interest. Some of these feeds have been studied by other groups, but none of the studies in the literature have examined the hydrocarbon pools.\textsuperscript{2,14,15,60-62} Water was used as a diluent to keep the carbon molar flow rate consistent between different feeds. These experiments used H-ZSM-5 with a Si/Al ratio of 40. To better approximate the operating conditions of a commercial plant, these experiments were done at a pressure of 10 bar at 400°C.\textsuperscript{63,64} All feeds resulted in nearly identical gaseous product distributions after two hours on-stream, as shown in Figure 15.

Methanol-ethanol mixtures

The compositions of the gaseous effluents over time as the catalyst deactivated are shown in Figures 16-18. Figure 16 shows the gas products from a 90:10 mixture of methanol:ethanol, while Figures 17 and 18 show the gas products from a 50:50 mixture. Not surprisingly, the 90:10 mixture gas profile resembles the methanol profile in Figure 11, with a difference of a slower decrease in ethylene production during deactivation. Similarly, the 50:50 mixture produces much more ethylene during deactivation than the 90:10 mixture. The dominant retained species from a mixture of methanol and ethanol were xylenes, trimethyl benzene, tetramethyl benzene and pentamethyl benzene. No polyethyl benzenes or mixed methyl/ethyl benzenes were present in appreciable amounts. Interestingly, analysis of the found in ETG was suppressed when methanol was mixed with ethanol. The reason for this is unknown at this time.
Figure 15. Gaseous products from reactions over H-ZSM-5 at 400°C, 10 bar.
Figure 16. Light olefins and paraffins produced from a 90:10 carbon molar ratio of methanol/ethanol at 400°C, 10 bar.

Figure 17. Light olefins and paraffins produced from a 50:50 carbon molar ratio of methanol/ethanol over H-ZSM-5 at 400°C, 10 bar.
Figure 18. Gaseous products from a 50:50 carbon molar ratio of ethanol/methanol feed over H-ZSM-5 at 400°C, 10 bar.

Isopropanol

The zeolites used for an isopropyl alcohol feed contained a mixture of methyl benzenes, ethyl benzenes, mixed methyl ethyl benzenes and trimethyl propyl benzenes. The gaseous and liquid products were consistent with those from the methanol and ethanol runs. Deactivation of the catalyst was significantly slower when isopropanol was used as the feed than when methanol or ethanol was used as the feed, when compared on a constant carbon molar flow rate. As the catalyst was deactivated by coking, the amount of propylene formed from the dehydration of propanol increased, in a similar manner as the dehydration of ethanol into ethylene. The changes in the levels of the gaseous products with time are shown in Figures 19 and 20. The figure shows that the gas concentrations are much more stable with
this feed than with ethanol or methanol. When a mixture of isopropanol and methanol was used, the formation of the ethyl benzenes and trimethyl propyl benzene was suppressed. This behavior was similar to the suppression by methanol of the formation of ethyl benzenes and mixed methyl ethyl benzenes from ethanol as shown in Figure 21.

![Graph showing area vs time for various hydrocarbons](image)

**Figure 19.** Light olefins and paraffins produced from isopropanol at 400°C, 10 bar.
Figure 20. Gaseous products from isopropanol feed at 400°C, 10 bar.

Acetone

To get a better understanding of the behavior of the isopropanol feed, acetone was also studied due to the similar structure, differing from isopropanol in the oxidation state of the second carbon atom. The used zeolites contained mostly methyl benzenes and some mixed methyl ethyl benzenes, as shown in Figure 22. The retained material was similar to that found in the zeolites used for MTG, with the main difference of the presence of significantly more ethyl dimethyl benzene from acetone than found from methanol and the presence of trimethyl propyl benzene as found in the isopropanol process. One difference between the acetone feed’s retained material and those of the methanol and isopropanol was the presence of the dimethyl naphthalene and trimethyl naphthalene. These naphthalenes are more commonly found after longer times on-stream and are associated with coke formation. It is unknown why these species were present; further deactivation studies are needed to
confirm this behavior. Again, the gaseous and liquid products after two hours on-stream were consistent with those from the methanol and ethanol runs.

![Diagram showing GCMS of retained material within H-ZSM-5, 400°C, 10 bar.](image)

**Figure 21.** GCMS of retained material within H-ZSM-5, 400°C, 10 bar.
Figure 22. GCMS of retained material within H-ZSM-5, 400°C, 10 bar.
**Tertiary butyl alcohol**

The zeolites used for a $t$-butanol feed contained a mixture of methyl benzenes, ethyl benzenes, mixed methyl ethyl benzenes, $m$-propyl toluene and butyl benzenes, as shown in Figure 22. These results are consistent with the trend found with the other alcohols, where all retained material contains methyl benzenes and benzenes with alkyl groups of the same number of carbons as the feed alcohol, along with alkyl groups of intermediate sizes. Again, the gaseous and liquid products were consistent with those from the methanol and ethanol runs. Subsequent experiments showed when $t$-butanol is the feed, the zeolite deactivates more slowly.

**Benzyl alcohol**

When benzyl alcohol was fed to the process, the catalyst coked rapidly, to such an extent where the screen on which the zeolite rested became completely plugged after a few hours. The extent of coking was so severe that no retained material could be extracted from the zeolite. However, the gaseous and liquid products after two hours on-stream were still consistent with those from the methanol and ethanol runs.

**Conclusions and Future Work**

Although the gas and liquid products of the different alcohol feeds are nearly the same, the composition of the material retained in the zeolite clearly depends on the feed. Methyl benzenes are the dominant species in the hydrocarbon pool within H-ZSM-5 and are retained within the zeolite using any alcohol feed. Higher alcohols fed to the process create aromatic rings within the pores with alkyl chains of the same number of carbons in addition to shorter alkyl chains. However, the various alkylated benzenes that differ between
processes do not appear to have much of an effect on the reactor effluent. The reason for the similarities in composition is believed to be that the most active components of the hydrocarbon pool are the methyl benzenes common to all of the processes. The retained higher polyalkyl benzenes that differ between feeds are believed to be less reactive. The differences between feeds to this process become most apparent as the catalyst deactivates and the hydrocarbon pool pathway becomes less significant. One of the most interesting results of this study was that mixing methanol with a higher alcohol suppresses the formation of alkylated benzenes typically found retained in the pores of the catalyst when the higher alcohol is the sole organic in the feed. The reason for this is unknown, suggesting that the hydrocarbon pool mechanism is still not well-understood and requires further study. An understanding of this behavior would provide valuable insight into the MTG and general ATG mechanism. This project is being continued by two graduate students at CSG. They are running more deactivation tests, including acetone and $t$-butanol. Studies with mixtures of alcohols where one alcohol is isotopically labeled are currently under consideration. These studies can indicate how the two different alcohols are incorporated into the aromatic compounds found retained in the zeolite. This analysis may shed some light on the mechanism behind methanol’s suppression of the formation of higher polyalkyl benzenes. Additionally, isotopic studies with higher alcohols may reveal support for or opposition to the dual cycle proposed by Bjørgen et al. for the MTG process.

References


Appendix 1. Controlled Spacing and Cooperative Catalysis

Introduction

The effectiveness of a cooperative catalyst depends on the spacing and orientation of the functional groups. Acid-base pairs must be carefully incorporated so that they are close enough for catalysis, yet far enough to prevent negative interactions such as the formation of zwitterions. Cooperative catalysis by silica materials mentioned earlier generally results from a broad distribution of spacings between the acid and base groups. Not only do active sites increase the reaction rate, but the spacing between the catalytic groups also can determine selectivity and chirality.

Consider a cellulase enzyme that contains an active site consisting of a pair of amino acids, a protonated glutamic acid residue and a glutamate residue.⁰ There are two types of cellulolytic enzymes with different mechanisms of enzymatic glycosidic bond hydrolysis that were originally proposed by Koshland²: inverting and retaining, referring to the final configuration of the glycosidic oxygen atom being equatorial (retained) or axial (inverted). The cooperative catalysis of the acid-base pair lowers the activation energy of hydrolysis. In both mechanisms, shown in Figure 1, the acid protonates the glycosidic oxygen atom. In the retaining mechanism, the basic residue forms a covalently bonded intermediate with the first carbon while the base in the inverting mechanism activates a water molecule for a nucleophilic attack on the first carbon. In this type of cellulase, the residues are 4.8-5.3 Å apart. Correspondingly, the inverting mechanism requires a larger distance between the residues, 9.0-9.5 Å, to accommodate both a cellulase segment and a water molecule.²
The goal of this project was to synthesize heterogeneous catalysts with organic functional groups where the distance between the groups is controlled and show cooperativity in a reaction based on an enzymatic mechanism. This would be done by incorporating the moieties into the same molecule, which, in turn, can be linked to a silane in order to be incorporated into mesoporous silica. The effect of the spacing between the catalytic groups would also be studied.

Mbaraka and Shanks\textsuperscript{4} co-condensed dipropyl disulfide groups into SBA-15, where the disulfide bond was cleaved in acidic medium to generate sulfonic acid pairs with spacing uncommon for randomly co-condensed propylsulfonic acid groups.\textsuperscript{4,5} The authors found that these proximal pairs displayed greater acid strength than isolated sulfonic acid groups.\textsuperscript{4} However, when testing catalytic activity of sulfonic acids derived from disulfides, the results may be misleading if not all of the disulfides are converted to sulfonic acids. Such was the case for Dufaud and Davis,\textsuperscript{6} who proposed cooperativity between two proximal sulfonic acid groups on SBA-15 in the synthesis of bisphenol A from acetone and phenol. Zeidan et al.\textsuperscript{7} later demonstrated that the activity observed in the Dufaud study was instead due to
cooperative catalysis by thiol-sulfonic acid pairs, where the thiol acts as a nucleophile. These proximal sites were also found to shift the selectivity of the reaction.

Margelefsky et al. synthesized SBA-15 functionalized with catalytic pairs of sulfonic acid and thiol groups via opening of a 1,3-propanesultone ring and used the material to catalyze the synthesis of bisphenol A. The authors were able to vary the distance between functional groups and found that there was an optimal spacing for both activity and selectivity.

Two different catalyst systems for the hydrolysis of cellobiose were studied: a homogeneous acid tetramer and a bifunctional acid-base mesoporous silica catalyst. The acid tetramer study was an investigation into proximity effects between four acids in a ring structure. The goal of the mesoporous silica study was to develop a synthetic, heterogeneous analogue to cellulase enzymes as an alternative, cooperative acid-base catalyst.

**Acid-base functionalized mesoporous silica**

SBA-15 was the type of silica chosen due to its large pores and its higher hydrothermal stability than other mesoporous silicas. The acid-base pair chosen for random incorporation via co-condensation was a carboxylic acid group and a primary amine group. Both of these moieties have been successfully incorporated into SBA-15 in the literature. The butylcarboxylic acid moiety is obtained by oxidation of a co-condensed cyanopropyl moiety. The butylcarboxylic acid moiety was chosen for this acid-base pair due to its similarity to the acid moieties in cellulase enzymes. Although the butylcarboxylic acid is unable to catalyze cellobiose hydrolysis on its own, in principle, it could likely catalyze this reaction when
acting in a cooperative manner with a basic moiety. Use of a stronger base might actually inhibit cooperative catalytic activity if the acid and base can easily form zwitterions.

**Experimental**

All chemicals were used without further purification. The structure-directing agent, Pluronic P123 (BASF Co.), (4 g) was dissolved in 125 ml deionized water and 25 ml hydrochloric acid (12.1 N). Tetraethoxysilane (TEOS) was added as the silica precursor (98%, Acros Organics) at 40°C. An hour was allowed for prehydrolysis before cyanopropyltriethoxysilane was added (CPTES, Gelest). 3-Aminopropyltriethoxysilane (APTES, Gelest) was added 15 minutes after the addition of CPTES. The solution was stirred at 40°C for 20 hours, and then aged in a 90°C oven for 24 hours. The solution was then filtered and allowed to dry at room temperature overnight. The Pluronic P123 was removed from the pores by refluxing in ethanol and HCl, followed by filtration. The cyano groups were hydrolyzed to carboxylic acid groups by refluxing in sulfuric acid and water and followed by filtration.

**Catalytic testing**

Cellobiose hydrolysis experiments were carried out in a Parr 300-mL stainless steel batch reactor, mixed with an impeller and maintained at 150°C using a heating jacket and internal cooling water loop. Samples of the reaction mixture taken during the reaction were analyzed using an Agilent 1050 high-pressure liquid chromatograph equipped with a refractive index detector.

**Results and discussion**

The amine-carboxylic acid functionalized SBA-15 was successfully synthesized with the functional organosilanes incorporated into the catalyst, prior to the first report in the
literature of the same organic moiety combination in co-condensed SBA-15. The percent functionalization of this catalyst was determined by $^{29}$Si MAS NMR, the spectra of which is shown in Figure 1. This analysis was done by Ram Kanthasamy and Dr. Sarah Larsen at the University of Iowa. Table 1 shows that the silica percent functionalization of the bifunctional SBA-15 is approximately the sum of the percents of functionalization of the two monofunctionalized silicas. Both moieties were successfully identified by solid-state $^{13}$C CP MAS NMR. The carbon spectra are shown in Figure 2. The peak at 283 ppm was assigned to the carboxylic acid carbon, and the peaks at 14, 25 and 46 ppm were assigned to the aminopropyl carbons.\(^9\)

**Figure 1.** $^{29}$Si MAS NMR spectra of functionalized SBA-15.
Table 1. Functionalization of SBA-15 determined by $^{29}$Si MAS NMR.\textsuperscript{9}

<table>
<thead>
<tr>
<th>Functionalized SBA-15</th>
<th>% Functionalization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butylcarboxylic acid (BC)</td>
<td>8.8%</td>
</tr>
<tr>
<td>Aminopropyl (AP)</td>
<td>8.2%</td>
</tr>
<tr>
<td>Bifunctionalized (AP+BC)</td>
<td>15%</td>
</tr>
</tbody>
</table>

**Figure 2.** $^{13}$C CP-MAS NMR spectra of functionalized SBA-15.

Incorporation of the amine group was also confirmed by elemental analysis. Initial synthesis attempts were unsuccessful due to insufficient TEOS, which resulted in a gel rather than a powder. When the amount of TEOS in the synthesis solution was increased, good structural order was apparent in the narrow pore size distribution determined from nitrogen desorption as shown in Figure 3. This catalyst had an average pore diameter of 60 and a specific surface area of 600 m$^2$/g.
This acid-base catalyst was not active in the hydrolysis of cellobiose. Neither the acid nor the base was able to catalyze the reaction singly, as well. Acid-base reactions in water are complicated by proton mobility, whereby the two functional groups can neutralize each other, or the proton may not remain in the vicinity of the acid-base pair for effective cooperative with the base moiety. As a result, acid-base cooperativity in aqueous systems reported in the literature generally uses a buffer to maintain the desired acid protonation and base deprotonation. However, use a buffer defeats many of the advantages of using a heterogeneous catalyst. To avoid the solvent effects of water, the same catalyst was tested with a Knoevenagel condensation reaction, which has been shown to be cooperatively
catalyzed by propylamine-functionalized silicas.\textsuperscript{10} As discussed in Chapter 3, and in the paper published by Bass et al.\textsuperscript{10} that the Chapter 3 study complements, the propylamine moiety acts in concert with surface silanol to attain a higher reaction rate than when it is unsupported. Consequently, it appeared that the Knoevenagel condensation would be a feasible test case for the butylcarboxylic/aminopropyl-functionalized SBA-15. However, the bifunctional catalyst did not display different activity – better or worse – than the singly functionalized aminopropyl SBA-15. The butylcarboxylic acid moiety did not demonstrate catalytic activity when singly supported on SBA-15. Different functional group loadings with varying proportions of the acid to base also had no effect. Additionally, different catalyst preparation methods were tried, such as the usual base treatment with tetramethylammonium hydroxide, no base treatment, thorough water washings, and adjustment of the pH by acid or base followed by filtration, yet all failed to produce acid-base cooperativity effects. It is unclear why the Knoevenagel condensation was an unsuccessful test case for acid-base cooperativity using the butylcarboxylic group as the acid.

**Proximity effects**

The Katz research group at the University of California – Berkeley synthesized a calixarene, a ring of four benzene rings with sulfonic acid groups, shown in Figure 4. This homogeneous catalyst was used to catalyze the hydrolysis of cellobiose with a comparison to a \(p\)-phenolsulfonic acid monomer. The goal of the study was to see if there is a difference in acidity and catalytic activity of the sulfonic acid groups when in proximity with one another. These experiments followed the same procedure as the cellobiose hydrolysis using the acid-base functionalized SBA-15. Both the calixarene and the monomer were active in the
hydrolysis of cellobiose. However, due to the leveling effect of water, where strong acids dissociate completely, forming hydronium ions, no significant difference in catalytic activity was observed between the monomer and the calixarene. The apparent first order rate constants per mole of acid group are shown in Table 1. As a result of this study, the project focus was shifted to organic reactions and solvents due to the complex nature of water as a solvent.

**Figure 4.** Phenolsulfonic acid calixarene.

**Table 1.** Rate constants for cellobiose hydrolysis using a phenolsulfonic acid calixarene (Calix 1-3) and p-phenolsulfonic acid (1-7).

<table>
<thead>
<tr>
<th></th>
<th>k h⁻¹ mol acid⁻¹</th>
<th>Average</th>
<th>Std.dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12.1</td>
<td></td>
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</tr>
<tr>
<td>6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>13.6</td>
<td>12.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Calix1</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calix2</td>
<td>12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calix3</td>
<td>14.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calix1</td>
<td>12.1</td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>
Controlled spacing

This project involved collaboration with Dr. Bert Chandler’s research group in the chemistry department at Trinity University.\textsuperscript{11} His group worked on developing synthesis procedures for organic groups that can be linked to 3-iodopropyltrimethoxysilane (IPTMS) and be immobilized on mesoporous silica via grafting or co-condensation. These groups, referred to as “dimers,” can be a pair of acids or bases or an acid and a base. Additionally, if two acid groups are used, half of the acids can be titrated with a base to obtain an acid-base pair. A diacid is expected to have higher strength than a monoacid, as hydrogen bonding between one acid group and the oxygen atom of the neighboring acid group stabilizes the anion of that group, weakening the bond between the anion and the proton. The Chandler group worked on synthesizing different functional groups and backbones of varying lengths and determining distances between the functional groups, ranging from 2.5 Å to 14 Å.

Catalytic testing – preliminary results from the Chandler group

For catalytic activity testing, model reaction systems for which enzymatic activity have been characterized are of interest. Kilgore and Pickett\textsuperscript{11} synthesized a diacid dimer and used it in the homogeneous form to catalyze formation of a secondary amide bond at room temperature as a test reaction. Other reactions under consideration by Chandler’s group are amide bond hydrolysis, aldol condensations and carbon-carbon bond forming reactions. The Chandler group found that the condensation of formic acid ($pK_a$ 3.75) and diethylamine at room temperature proceeded to completion in less than 10 minutes when catalyzed by phthalic acid ($pK_a$ 2.96), the dimer with succinic acid ($pK_a$ 4.19) groups, or the dimer with maleic acid ($pK_a$ 2.00) groups.\textsuperscript{12} Monoprotic acids, on the other hand, hydrochloric acid and
acetic acid (pKₐ 4.74) were less active. HCl required over 24 hours to reach completion, whereas when acetic acid was the catalyst, the reaction reached completion in 0.5-3 hours.

![Figure 4. Backbone with succinic acid groups](image1)

![Figure 5. Backbone with maleic acid groups](image2)

**Catalyst synthesis**

The dimer can either be anchored to IPTMS prior to grafting, as done in the Chandler group, or the support can be synthesized first with co-condensed iodo groups, onto which the dimer is subsequently linked. The reaction pathway begins with an S_N2 reaction of triphenylphosphine with the iodo group. The dimer is subsequently anchored to the silane by a base-catalyzed Wittig reaction with the dimer ketone, releasing the triphenylphosphine and forming a double bond linkage. This series of reactions is shown in Figure 6. The structure of the dimer was confirmed by NMR spectroscopy by the Chandler group.
Figure 6. Dimer catalyst synthesis pathway
(A) Co-condensation of TEOS and IPTMS into SBA-15. (B) Triphenylphosphene $S_{N2}$ reaction. (C) Anchoring of dimer via Wittig reaction.
**Experimental plans**

The mesoporous silica support chosen was SBA-15 due to its large pores, which can easily accommodate the dimers being studied. The focus here is on co-condensation, which has several advantages over grafting, as discussed earlier, making SBA-15 the silica synthesis method of choice for this study. 3-Iodopropyltrimethoxysilane (IPTMS) has been grafted onto silica surfaces, but incorporation via co-condensation has been reported only recently. Iodo groups cannot be incorporated via co-condensation into MCM-41 or HMS silicas due to side reactions. The basic conditions of MCM-41 syntheses and the neutral amine surfactants of HMS syntheses leave the halide carbon vulnerable to nucleophilic attack in a S$_{N}$2 reaction (substitution, nucleophilic, bimolecular). The synthesis procedures used for the other organic-functionalized must be modified due to the vulnerability of the iodopropyl group to nucleophilic attack. When hydrochloric acid was used in the synthesis mixture, the suspension of particles became yellow to orange, indicating loss of iodine from the iodopropyl groups, due to exchange with chlorine in the acidic solution. However, simply treating the chloro groups with an excess of sodium iodide has been shown to be ineffective in restoring the iodo group. Use of sulfuric acid gave similar results, as iodine (pK$_a$-10) is a better leaving group than the sulfuric acid anion (pK$_a$ 1.99). Consequently, to avoid this problem, acid in the catalyst synthesis mixture should be replaced with hydrogen iodide (HI), with a method adapted from a study by Alauzun et al. The protons associated with oxygen atoms in the EO blocks during catalyst synthesis are accompanied by the acid anions to balance the charge, which affect the silica condensation rate. Consequently, condensation is expected to be accelerated by the use of HI, so a shorter prehydrolysis period than that commonly used for HCl-catalyzed SBA-15 syntheses.
In order to ensure the independence of the incorporated molecules the loading of the iodopropyl groups were to be kept low initially. Once synthesized, the goal was to study acid-base cooperativity, either with an acid-base functionalized dimer or an acid dimer with half of the groups titrated, effectively forming an acid-base catalyst. The dimer-functionalized SBA-15 would be used to catalyze one or more of the model reactions, for which turnover frequencies and kinetics would be obtained. The activity of the homogeneous dimer would be compared to the activity of the dimer-functionalized SBA-15 to determine any effects of the silica support. Future work may also include varying the length of the dimer backbone to determine the effect of proximity on catalytic activity. Unfortunately, the Chandler group encountered some difficulties when synthesizing these dimers, and the project was discontinued.

References

Appendix 2. Basicity and Catalytic Activity

The original goal of the study of new organic base-functionalized SBA-15 catalysts was to examine the link between basicity and catalytic activity. These new two bases, ethylpyridine-functionalized SBA-15 (EPS) and dihydroimidazole-functionalized SBA-15 (DHIS), as well as aminopropyl-functionalized SBA-15 for comparison, were shown to be catalytically active in a Michael reaction. This reaction was chosen because it is a simple reaction established in the literature with no significant byproducts and has been shown to be catalyzed by propylamine-functionalized silicas.\(^1\) SBA-15 functionalized with pyridine groups, the weakest of the three bases, appeared to be less active than the aminopropyl- and dihydroimidazole-functionalized silicas; however, this difference was not statistically significant. The DHIS was expected to be the most active catalyst, but it showed approximately the same activity as the APS. It was expected that apparent activation energies would vary with base strength, where EPS would have the highest activation energy as the weakest base and DHIS would have the lowest activation energy as the strongest base, with APS falling between. This trend appears to hold, with apparent activation energies of 10.6 kJ/mol for DHIS, 12.1 kJ/mol for APS and 17.8 kJ/mol for EPS. However, these apparent activation energies are quite low for a carbon-carbon bond forming reaction, so it is possible that mass transfer limitations play a role in the observed activity of these heterogeneous catalysts.

If the past reactions were mass transfer limited, it is possible that increasing the pore diameters will reveal a difference in the activity of the dihydroimidazole and aminopropyl groups. Consequently, catalysts with expanded pore diameters were synthesized by
increasing the time and temperature of the aging synthesis step and by using a pore-swelling agent and the catalytic testing was repeated. Increasing the time and aging temperature of the catalyst synthesis solution was found to have only a minor effect on pore size. An alternative method for enlarging pores is using mesitylene as a pore-swelling agent. This was added to the acidic solution after the Pluronic P123 was dissolved, prior to addition of tetraethoxysilane. The mesitylene was presumably removed along with the Pluronic P123 during refluxing ethanol extraction. Materials synthesized using this additive exhibited a less ordered structure, as shown by the nitrogen adsorption/desorption isotherms and pore size distributions. Additional complications were that these SBA-15 catalysts had more variance in the amount of incorporated bases and in the specific surface area. Reactions run with these materials did not indicate any differences between the activities of the bases. It appears that the Michael reaction was a poor test reaction for demonstrating a correlation between catalyst basicity and activity.

Amine characterization

A variety of titrations were attempted to determine the number and strength of the different amines: perchloric acid in acetic acid, back-titrations, and titrations using varied parameters, such as dosing frequency, titrant concentration, and pretreatment conditions (heating to 100°C under a vacuum of 10 μg Hg). None of these methods proved to be an effective way to consistently determine the number of active sites. Quantification of amines by potentiometric titration is complicated by the presence of silanols that can form zwitterions with the amine groups; acid added during a titration first protonates free amines, then the zwitterions. As a result, results of titrated organic base-functionalized mesoporous
silicas are rarely reported in the literature. Walcarius et al.\textsuperscript{3-5} also reported the greater difficulty of quantifying the base sites for mesoporous silica than for other types of silicas. This behavior is still not well-understood. These difficulties were motivation for the development of a ninhydrin assay by the Chandler group to quantify reactive amines.\textsuperscript{6}

References

The Hydrocarbon Pool in Ethanol-to-Gasoline over HZSM-5 Catalysts

Roger Johansson · Sarah L. Hruby · Jeppe Rass-Hansen · Claus H. Christensen

Abstract It is shown that the conversion of ethanol-to-gasoline over an HZSM-5 catalyst yields essentially the same product distribution as for methanol-to-gasoline performed over the same catalyst. Interestingly, there is a significant difference between the identity of the hydrocarbon molecules trapped inside the HZSM-5 catalyst when ethanol is used as a feed instead of methanol. In particular, the hydrocarbon pool contains a significant amount of ethylsubstituted aromatics when ethanol is used as feedstock, but there remains only methyl-substituted aromatics in the product slate.

Keywords Ethanol-to-gasoline · Hydrocarbon pool · ZSM-5

With the current development of new large methanol plants, including a 5000 ton/day plant recently opened in Saudi Arabia [1] and a 1500 ton/day plant under construction in Russia [2], the subsequent expected increases in available methanol and the cost competitiveness due to economics of scale are generating significant potential for the methanol to hydrocarbon (MTH) reaction to become an important industrial process in the coming years. Some existing plants are currently utilizing this route to produce olefins; one of the largest belongs to Viva Methanol Ltd. in Nigeria [3]. MTH or, depending on process conditions, methanol to gasoline (MTG) or methanol to olefins (MTO) can be used to produce liquid fuels for the automotive sector or to make olefins suitable for polymerization. The production of liquid fuels from natural gas via methanol was first commercialized by Mobil in the 1980s with a plant operating in New Zealand with a planned production of 600,000 tons annually. However, at that time the economy for the process was unfavorable due to low fossil fuel costs; consequently, the MTG part of the operation was discontinued in the 1990s. Today, the increasing prices of fossil feedstocks could once again make the MTG process a viable option. The MTG reaction was first discovered by Silvestri and Chang in the 1970s and it is catalyzed by acidic zeolites at temperatures up to 400 °C giving a variety of lower aliphatic hydrocarbons, olefins and aromatics [4]. The product distribution in MTG depends on several factors where, in particular, the topology of the catalyst is of paramount importance. Since its discovery, MTG has been extensively studied and a plausible reaction mechanism has been suggested through the work of several research groups [5, 6]. The basic premise for the proposed mechanism is the hydrocarbon pool model, which suggests that the actual catalytic sites in the zeolite are organic–inorganic hybrids consisting of cyclic organic species contained within the zeolitic framework. These organic species act as the hydrocarbon pool from which the products in the exit gas stem via cracking as shown in a simplified reaction scheme in Scheme 1. The MTG process has been extensively studied by Kolboe et al., who studied the nature and amount of retained material within the catalysts H-beta, [7–9] SAPO-34, [10, 11] and...
H-ZSM-5 [12, 13]. These authors gained considerable insight into the mechanism by determination of retained material in the used catalyst and many aspects of the hydrocarbon pool model stem from their work. The MTG process has a counterpart in the ethanol to gasoline (ETG) process, which gives an almost identical product distribution as the MTG process [14–16]. Since MTG and ETG most likely proceed through similar routes, the study of retained material in the ETG reaction could also provide interesting insight into MTG.

The amount of ethanol currently produced has increased significantly in recent years due to the rising demand for domestic, biorenewable alternatives to petroleum-based fuels and chemicals. There are many potential reactions utilizing ethanol to produce important chemical feedstocks [17] such as steam reforming to hydrogen, [18–20] dehydration to ethylene, [21] oxidation to acetaldehyde, [22] oxidation to acetic acid, [23, 24] and oxidation followed by condensation to butadiene [25]. Some of these aforementioned reactions, namely the processes leading to ethylene and butadiene, have been demonstrated on an industrial scale but have not retained their commercial importance when less expensive routes starting from fossil fuels have been implemented instead. The other processes mentioned above have mostly received attention in the last decade but have not found industrial applications yet. However, this might change in the near future, where commercialization of new (or old) process routes towards renewable chemicals could become industrially important along with the depletion of fossil resources. One of the present important drawbacks of the production of ethanol from biomass is the energy input required for distillation. Except in the case of sugarcane ethanol, where bagasse usually is used for the thermal energy generation, this energy generally comes from fossil resources. New ways of producing fuel grade ethanol like molecular sieves or membranes can decrease this energy input—though not avoid it. Consequently, when developing new reactions aqueous ethanol would be the preferred feedstock to achieve a more favorable energy balance by reducing the required extent of distillation. As a result, processes that do not require fuel-grade ethanol such as the dehydration of ethanol to ethylene and steam reforming to hydrogen are attracting interest [18, 26]. Other researchers have investigated the use of the ethanol to gasoline reaction as an alternative to fuel grade distillation of ethanol [27]. One challenge with the ETG process that can be envisioned when using ethanol as feed is a more rapid catalyst deactivation due to the formation of ethylene, which is a known coke precursor on H-ZSM-5 [28]. This deactivation could perhaps be inhibited by addition of water to the feed, [28, 29] using lightly distilled bio-ethanol as the feed would add additional water to the reaction and slow down deactivation and lower the ethanol feed concentration. Our first effort towards this is to study the mechanism behind ETG through the analysis of retained material in the catalyst after the ethanol to gasoline reaction. This has been done previously for the MTG reaction but to our knowledge no such information exists for the ETG reaction. We are also comparing the ETG and MTG reaction with the same process parameters to increase our understanding of these reactions and to examine possibilities of mixing crude bioethanol with methanol in a combined reaction whereby distillation of ethanol can be avoided.

The catalyst used in this study was H-ZSM-5 (Si/Al = 11.5), supplied by Zeolyst International. The experiments for determining retained material were performed in a continuous flow fixed bed quartz tubular reactor with an inner diameter of 6 mm; the catalyst bed was heated in an oven, the temperature monitored with a thermocouple situated immediately below the catalyst bed. The ethanol was added through a HPLC pump and then evaporated by heating tapes and carried through the catalyst bed with a flow of helium. The stream was then brought to an Agilent 6890 GC equipped with a Varian PoraPlot Q-HT column and a FID where the product distribution was analyzed. The experiments comparing ETG with MTG were performed on a similar setup but using a stainless steel reactor fitted with a condenser to separate gaseous products from condensable products before analysis on an Agilent 6890 GC equipped with a J & W Scientific GS-Gaspro column and a FID where the gaseous products were analyzed.

Experiments were carried out at 450 °C or 400 °C with a WHSV of 9 h⁻¹ or 6 h⁻¹ respectively. For the retained material study the reactor was heated to 450 °C and after 15, 60 or 120 min, the reactor was immediately moved to another oven where the catalyst was flushed with helium for 5 min at 55 °C to remove small molecules not trapped inside the zeolite pores.

For determining the retained material in the methanol to olefin process we have replicated the method employed by Guisnet et al. [30] in order to gain insight into the ethanol to gasoline reaction. In a closed Teflon vial 100 mg of spent catalyst was dissolved in 3 mL of 20% wt

![Scheme 1](image-url) A simplified scheme showing the principle behind the hydrocarbon pool model in the MTG reaction. Methanol reacts with hydrocarbons trapped inside the zeolite giving a charged organic–inorganic hybrid that then loses a smaller fragment giving back the same or a similar hydrocarbon
hydrofluoric acid. The mixture was shaken and allowed to stand overnight. When the zeolite was completely dissolved, the retained material was extracted with 1 mL of dichloromethane with added chlorobenzene as an internal standard. The organic phase was filtered and most of the dichloromethane was allowed to evaporate; Arstad et al. [10] have shown that this should not have an effect on the product distribution in the sample. The concentrated samples were then analyzed on an Agilent 6850 GC fitted with a quadruple mass spectrometer detector 5975C.

As it was stated previously, the products achieved from the MTG and the ETG processes are very similar; specifically the gaseous products are the same in both processes as can be seen in Fig. 1. Additionally the condensable products are similar although there are subtle differences between the two processes; Figure 2 gives spectra showing the main liquid products in the ETG and MTG respectively. In the MTG there are small amounts of trimethyl benzene and tetramethyl benzene that are not seen in ETG, in ETG there are instead small amounts of ethyl methyl benzene that is not found in MTG. These differences are not discernible using FID but can be seen when analyzing the samples with mass spectrometry. The similar product distribution for both processes suggests that

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**Fig. 1** Comparison of FID spectra of the gaseous products found in ethanol-to-gasoline reaction and methanol-to-gasoline run at 400 °C with a WHSV = 6 h\(^{-1}\). Spectra obtained after 2 h on stream

**Fig. 2** FID spectra showing the major condensable products in the ethanol-to-gasoline and the methanol-to-gasoline reactions at 400 °C with WHSV = 6 h\(^{-1}\). Spectra is showing the organic phase collected over the first 2 h of reaction
the same mechanism is in operation in both of these processes. If the same mechanism is in operation it would also be likely that the same material is retained within the catalyst. Figure 3 shows the most abundant retained material found in HZSM-5 for MTG and ETG respectively. When comparing the material released from the dissolved zeolite from the ETG reaction with the products in the reactor effluent it is apparent that the true retained material

![Diagram of retained material in HZSM-5](image)

**Fig. 3** The major compounds of retained material found within H-ZSM-5 after reaction with either methanol (a) or ethanol (b). Reactions run at 450 °C with WHSV = 9 h⁻¹. The truly retained compounds are depicted in the last row in the MTG and in the lower two rows in ETG.

**Fig. 4** Total ion chromatogram for the retained material in HZSM-5 after addition of ethanol at 450 °C with a WHSV of 9 h⁻¹ for a 15 min, b 60 min, and c 120 min. *Oxidized form of tetraethyl benzene due to the treatment with hydrofluoric acid.
consists of tetraethyl benzene, triethyl methyl benzene, triethyl benzene, diethyl dimethyl benzene, and diethyl methyl benzene, see Fig. 3, since these compounds are not present in the reactor effluent. Many of the smaller methyl benzenes such as the xylenes are present in both reactions and are expected to lead to the same products. In the catalyst from the ETG reaction there are several mixed methyl ethyl benzenes that are similar to the methyl benzenes found in MTG but it is surprising that these mixed benzenes give the same product distribution as the hydrocarbon pool containing only methyl benzenes. A more thorough examination of the results from experiments with different reaction times revealed that the amounts of tetraethyl benzene, triethyl methyl benzene, and triethyl benzene were increasing over time whereas the amount of methyl benzenes were approximately the same throughout, as seen in Fig. 4. This implies that the methyl benzenes that are common for both reactions are reacting faster than the ethyl benzenes present in the ETG reaction. Considering that the most reactive species of the hydrocarbon pool are shared between the two processes it is not so surprising that the product distribution is almost the same in both processes, the differences in product distribution should therefore come from those species that are not shared between ETG and MTG. Special attention should be given to the peaks corresponding to triethyl methyl benzene and tetraethyl benzene; these appear to be increasing more than any of the other peaks over time and it is reasonable to believe that these do not participate significantly in the reaction and could be considered as “dead ends” in the reaction network, similar to what Bjørgen et al. found for hexamethyl benzene in HZSM-5 for the MTG reaction [12]. If the triethyl methyl benzene and the tetraethyl benzene are true dead ends, as the time study suggests, they would be left unchanged by a flushing experiment at the reaction temperature, in this paper 450 °C. When flushing the catalyst at 450 °C a substantial decrease in the amount of tetraethyl benzene and triethyl methyl benzene is apparent, but at this time it is not clear why these species are decreasing. This behavior could mean that these species are indeed part of the reaction network, although at a slower rate than the smaller species in the hydrocarbon pool or they could be transformed into coke. When examining the catalysts used in reactions for longer times there are visible traces of the early stages of coke formation, which could be a logical progression from tetraethyl benzene and triethyl benzene. Whether these two species are reacting slowly or are coke precursors is inconsequential to the overall reactivity—either way the product distribution will not depend much on the larger species in the hydrocarbon pool.

The catalyst appears to deactivate faster with the formation of these compounds that potentially block the acidic sites within the zeolitic framework, thereby opening a second route towards deactivation apart from the coke formation on the surface of the zeolite crystals as has been seen by others in reactions with ZSM-5 catalysts [31, 32]. When performing deactivation runs using either ethanol or methanol as the feed it was seen that the ethanol feed gives a faster deactivation than the methanol feed. The deactivation in MTG is seen as a decrease of all products and formation of dimethyl ether, for the ETG reaction the deactivation manifests itself as an increase in the amount of ethylene forming from dehydration of ethanol whereas the other products are decreasing. The faster deactivation could be a consequence of the formation of the larger species found in the retained material in addition to the coke formation due to ethylene that was mentioned previously. From the present study it seems unlikely that ETG process in itself will ever get any commercial value. The process of converting one relatively low-value fuel into a more attractive fuel has to be exceptionally cheap to be economically viable, but the process might give some fundamental insight into the reaction mechanism of the MTG process. Moreover, a combined run where bioethanol is mixed with methanol in a possible MTG plant could find industrial importance.

In conclusion it is reasonable that MTG and ETG give similar product distributions since the products mostly stem from the same retained material via the hydrocarbon pool model, the difference in product distribution seen for the liquid products can be explained by the presence of larger hydrocarbon species found in the zeolite but which are not completely retained. In essence the formation of ethyl benzenes have small effects on the products formed but it could have implications for catalyst activity and deactivation. These issues are however expected to be less critical when a more dilute ethanol-water mixture is used. With the almost identical product distributions for the MTG and ETG experiments it is logical to conclude that one possible way of utilizing bioethanol, without distilling it to fuel grade ethanol, is to mix it with methanol, available from upcoming methanol plants, for a combined run. Thus, methanol mixed with some crude bioethanol can in a combined run be converted to a gasoline product in a METG process or alternatively to olefins (a likely more valuable product) in a METO process by altering the process conditions slightly.

References

Preparation and Characterization of Supported Amine Catalysts

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Abstract

Anchored amine materials can be prepared through a number of synthetic methodologies. Because of the potential importance of these materials to organic synthesis, a ninhydrin assay was developed as a rapid laboratory determination of available surface amines. The assay agreed well with expected values for aminopropyltriethoxysilane grafted onto commercial silica. The assay also distinguished between reactive amines and protonated or poisoned surface amines on co-condensed SBA-15 materials.

Introduction

Supported amine materials are being investigated as catalysts for a number of important organic reactions including Michael additions,¹² Knoevenagel condensation,³ aldol condensations,⁴,⁵ and cyano-O-ethoxycarbonylation.⁴ For many reactions, controlling the spacing between surface amine groups, or between amine groups and complementary functional groups, is important. A variety of synthetic methodologies are now emerging to exact this control; in many cases, substantial reactivity enhancements are observed when amine spacing can be carefully controlled.⁵⁻⁹

We have been developing methods to prepare and characterize supported amine catalysts using readily available commercial supports. One potential means of depositing amines on oxide surfaces is shown in Scheme 1, in which the micelle’s role is to space the amines on the surface. Current work is directed towards characterizing these samples, particularly applying fluorescence resonance energy transfer (FRET) techniques.

Determining the number of reactive surface amines is important for FRET measurements and for evaluating catalytic activities of supported amine catalysts. Elemental analyses give total nitrogen content, but an alternative that would only measure available amine groups would be more relevant for characterization catalytic materials. Traditional aqueous¹⁰,¹¹ and non-aqueous⁶ acid-base titrations are complicated by the buildup of surface charges, which shift pKa values and require extremely long (24+ hours) equilibration times.¹⁰,¹¹ For organic reactions that deal
with potentially large substrates or reaction products (e.g. from coupling reactions), it is also important to distinguish amines that can readily react with larger substrates from those that may be occluded in micropores or are otherwise inaccessible. As a first step in evaluating new supported base materials, we set out to develop a simple, fast assay for surface amines that could be used to quickly quantify the number of accessible amines in a typical research laboratory.

**Experimental Section**

**Materials.** 1,1,3,3-tetramethyldisilazane (Gelest), 3-indolepropionic acid (Aldrich Chemical Co.), aminopropyltriethoxysilane (Gelest), cetyltrimethylammonium bromide (Aldrich Chemical Co.), and ninhydrin (Aldrich Chemical Co.) were all used without further purification. Davicat SI-1403 silica powder (245 m²/g) was supplied by Grace-Davison. Water was purified to a resistivity of 17-18 MΩ-cm with a Barnstead Nanopure system. TRIS buffer (5 mM) was prepared using Tris-HCl and nanopure water, adjusting the buffer to pH 8.2 using dilute sodium hydroxide solution. Phosphate buffer (100 mM) was prepared using NaH₂PO₄ and Na₂HPO₄·7H₂O, adjusting the pH to 6.5. Solution UV-visible absorption spectra were collected using a Jasco V-530 spectrophotometer.

**Preparation of Grafted Amine-Functionalized Silica.** Silica was pressed, crushed, and sieved to 40-60 mesh particles and calcined at 550°C overnight. To anhydrous toluene (40 mL), silica (1.0 g) was added under N₂ and stirred for an hour. Aminopropyltriethoxysilane (APS; 1.0 g, 5.58 mmol) was syringed into mixture and stirred for 24 hours at room temperature under nitrogen. The functionalized silica was then filtered, washed with toluene three times, and dried under vacuum at 50°C.

**Silica Alkylation.** To tetramethyldisilazane (TMDS, 1.0 g) in anhydrous toluene (30 mL), amine-functionalized silica was added and stirred overnight at room temperature under N₂. The was then filtered, washed with toluene three times, and dried under vacuum at 50°C. Ethanol (190 mL) and nanopure water (10 mL) were mixed, and the pH was adjusted to 4.7 with acetic acid. Isobutyltrimethoxysilane (4.0 mL) was added to the solution, stirred for five minutes, and the modified silica was added. After ten minutes, the solution was decanted, the solid was washed with ethanol, cured at 110°C for ten minutes, and dried under vacuum.

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**APS-SBA-15 synthesis.** SBA-15 materials were prepared as described in the literature. The structure-directing agent, Pluronic P123 (BASF Co.), was dissolved in 125 ml deionized water and 25 ml hydrochloric acid (12.1 N) with stirring. Tetraethyl orthosilicate (TEOS) was added as the silica precursor (98%, Acros Organics) at 40°C. 3-aminopropyltriethoxysilane (APS) (99%, Aldrich) was added after a TEOS prehydrolysis period of one hour. The resulting mixture (1 TEOS: 0.1 APS/IPTES: 7.76 HCl: 171 H₂O molar ratio) was stirred at 40°C for 20 h and aged at 90°C for 24 h before being filtered. The surfactant template was removed by refluxing in ethanol with 10% hydrochloric acid for 24 h. The catalyst was then filtered and washed with ethanol. Excess protons from the acidic synthesis conditions were removed with 5 ml tetramethylammonium hydroxide (TMAH) solution (25 wt. % in methanol, Acros Organics) in 45 ml methanol with stirring for 30 min. The solid was filtered, washed 3x with methanol, and dried under vacuum.

**Ninhydrin Assays.** Ninhydrin tests were performed using a modified procedure of Taylor, et al. APS Silica (10-75 mg) of various loadings (0.857, 0.571, and 0.343 mmol NH₂/g Silica) was added to phosphate buffer (5 mL, 100mM, pH 6.5), and 1 mL of a 5% w/v solution of ninhydrin in ethanol was added to the slurry. After stirring for an hour in a boiling water bath, the mixture was allowed to cool slowly to room temperature. The silica was then filtered and washed three times with 70°C distilled water. The filtrate was collected, added to a volumetric flask, diluted to 100 mL, and the absorbance of this solution at 565 nm was measured using a UV-visible spectrophotometer. The reference solution was prepared as above with unmodified amine-free silica. Calibration standards were prepared with aliquots of a 1 mg/mL solution of APS in ethanol.

**Results and Discussion**

**Ninhydrin Assays of Grafted Silicas.** The reaction between ninhydrin and a primary amine, based on the work by Taylor and Howard, is shown in Scheme 2 (assay details can be found in the experimental section). For a surface titration, this reaction is advantageous because it cleaves the C-N bond of primary amines, resulting in a soluble highly colored analyte. The production of an extended aromatic product, along with three equivalents of water provides the strong driving force necessary to cleave the C-N bond. Calibration curves prepared with APS were linear and could be prepared daily for direct comparison with anchored amine materials. Figure 1 shows the results of ninhydrin assays of grafted, alkylated silica samples with various amine loadings. The first sample was repeated on different days (4 times each day) with freshly prepared solutions to show day-to-day reproducibility.
Figure 1. Ninhydrin tests on grafted APS silica materials. The two samples with 0.857 mmol/g loadings were tested using different solutions on different days to test reproducibility from day-to-day.

Table 1. Ninhydrin assays for surface amines using grafted silicas. a Determined from grafting synthesis and elemental analysis; b Typical standard deviations were 0.08 mmol N/g.

<table>
<thead>
<tr>
<th>Grafted Davisil</th>
<th>Expected Loading a (mmol N/g)</th>
<th>Experimental Results b (mmol N/g)</th>
<th>Error (mmol N/g)</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davisil A</td>
<td>0.86</td>
<td>0.86</td>
<td>0</td>
<td>0.4%</td>
</tr>
<tr>
<td>Davisil A</td>
<td>0.86</td>
<td>0.90</td>
<td>0.04</td>
<td>5%</td>
</tr>
<tr>
<td>Davisil B</td>
<td>0.52</td>
<td>0.48</td>
<td>0.04</td>
<td>7%</td>
</tr>
<tr>
<td>Davisil C</td>
<td>0.34</td>
<td>0.26</td>
<td>0.08</td>
<td>23%</td>
</tr>
</tbody>
</table>

Ninhydrin assay data for the grafted silicas is compiled in Table 1. The typical errors in the ninhydrin assays were within one standard deviation of the actual value, and the % errors were generally less than 10%, indicating that the assay gave reasonable results. The lowest amine loading had slightly larger errors, which is expected due to the lower total nitrogen content.

Ninhydrin Assays of Amine Functionalized SBA-15 Materials. The ninhydrin assay can also be used to enhance traditional elemental analysis, as it can distinguish between total N content and available/free amines. The latter are, of course, of primary concern for catalysis, and the assay offers an opportunity to distinguish between amines that readily react with organic molecules and those that may be protonated, occluded in the material, trapped in micropores, or poisoned by remnants of synthetic templates. SBA-15 materials, which are prepared using an oxide polymer template, make for a good test of the ninhydrin assay because they require polymer removal. For APS-SBA-15 materials, where the amine is incorporated during the SBA-15 synthesis, the polymer cannot be calcined without destroying the amine functionality. Less forcing conditions are therefore necessary, and it is important to confirm the availability of the remaining surface amines.
Figure 2. Ninhydrin tests on APS-SBA-15 performed after treatment in refluxing ethanol and after an additional treatment with N(CH₃)₄OH in refluxing methanol. Ninhydrin tests are compared to the expected results determined from elemental analysis.

Table 2. Ninhydrin assays for surface amines on APS-SBA-15 materials.

<table>
<thead>
<tr>
<th>SBA Material</th>
<th>N Loading b (mmol N/g)</th>
<th>Acid Reflux c (mmol N/g)</th>
<th>Base Treatment d (mmol N/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS-SBA-15 A</td>
<td>1.0</td>
<td>0.48</td>
<td>1.0 ± 0.17</td>
</tr>
<tr>
<td>APS-SBA-15 B</td>
<td>0.27</td>
<td>0.09</td>
<td>0.24 ± 0.06</td>
</tr>
<tr>
<td>APS-SBA-15 C</td>
<td>0.23</td>
<td>0.06</td>
<td>0.21 ± 0.02</td>
</tr>
</tbody>
</table>

The ninhydrin assay clearly shows that only a fraction of the total amines react with ninhydrin, suggesting that most of the amines are either protonated (and therefore unreactive) or poisoned by polymer remnants. Treating the materials with N(CH₃)₄OH removes any excess protons and may help to dislodge the any remaining polymer from the solid. The ninhydrin assay, which can be readily applied without scrupulously excluding water (e.g., with glove box or Schlenk techniques) readily distinguishes between reactive and unreactive amines and provides a relatively rapid amine analysis that can be readily performed in a synthetic laboratory.

Conclusions

A relatively simple, fast assay for accessible surface amines was developed using ninhydrin to oxidize an anchored primary amine and cleave the C-N bond. The highly colored aromatic species that is liberated from this reaction was readily analyzed with UV-visible spectroscopy and was compared to calibration curves prepared from aminopropyltrimethoxysilane. The ninhydrin assay was generally in good agreement with known values for amines grafted onto commercial silica and mesoporous SBA-15 materials that had amines incorporated into the mesopores during synthesis. Ninhydrin assays of the SBA-15 materials also distinguished
between functional and unreactive amines, and highlighted the importance of a base treatment after polymer removal if active amines are desired. This assay will aid in future characterization schemes and provides a rapid means of evaluating catalytic activity on a per amine basis.

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References


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15.
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