Fundamental studies of supported bimetallic catalysts by NMR spectroscopy

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Fundamental studies of supported bimetallic catalysts by NMR spectroscopy

Nilesh R. Savargaonkar

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

DOCTOR OF PHILOSOPHY

Department: Chemical Engineering
Major: Chemical Engineering
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1996
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Nilesh R. Savargaonkar

has met the dissertation requirements of Iowa State University

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For the Major Department

Signature was redacted for privacy.
For the Graduate College
To my mother, Usha Savargaonkar and father, Ramakant Savargaonkar who inspired me to reach higher goals and gave me moral support to struggle for achieving my goals
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Characterization of a bimetallic catalyst in terms of its surface composition is important in understanding the mechanisms of reactions over such catalysts. Since catalytic surfaces are covered with adsorbates under reaction conditions, the influence of adsorbates on the surface compositions of bimetallic catalysts is also important. Hydrogen was found to influence the surface compositions of silica and alumina supported Pt-Rh catalysts to a certain extent as the surfaces of bimetallic catalysts were enriched in Rh under the influence of hydrogen. Although the extent of Rh enrichment of the surface was not large, the surface compositions in the presence of hydrogen were significantly different from those of an adsorbate-free Pt-Rh surface which is known to be enriched in Pt.

Various hydrogenation reactions on transition metals are important commercially whereas certain hydrogenolysis reactions are useful from fundamental point of view. Understanding the hydrogen mobility and kinetics of adsorption-desorption of hydrogen is important in understanding the mechanisms of such reactions involving hydrogen. The kinetics of hydrogen chemisorption was studied by means of selective excitation NMR on silica supported Pt, Rh and Pt-Rh catalysts. The activation energy of hydrogen desorption was found to be lower on silica supported Pt catalysts as compared to
Rh and Pt-Rh catalysts. It was found that the rates of hydrogen adsorption and desorption on Pt-Rh catalyst were similar to those on Rh catalyst and much higher as compared to Pt catalyst.

The Ru-Ag bimetallic system is much simpler to study than the Pt-Rh system and serves as a model system to characterize more complicated systems such as the K/Ru system. Ag was found to decrease the amounts of adsorbed hydrogen and the hydrogen-to-ruthenium stoichiometry. Ag reduced the populations of states with low and intermediate binding energies of hydrogen on silica supported Ru catalyst. The rates of hydrogen adsorption and desorption were also lower on silica supported Ru-Ag catalyst as compared to Ru catalyst. Thus Ag influenced the kinetics and thermodynamics of hydrogen chemisorption on Ru particles and it was found that electronic and ensemble effects were not responsible for this influence of Ag. Instead, the effect of silver was due to the selective segregation of silver to the edge, corner and other defect-like sites which are proposed to be highly active for dissociative hydrogen adsorption. Hence hydrogen adsorption on Ru particles was found to be structure sensitive.
CHAPTER 1. GENERAL INTRODUCTION

Supported bimetallic catalysts are commonly used for commercial chemical reactions because these catalysts usually have higher activity, selectivity or stability as compared to monometallic catalysts (1–3). The modification of catalyst properties is most commonly explained via electronic (ligand) effects or geometric (ensemble) effects. In the case of electronic effects in bimetallic catalysts, one metal in the neighborhood of active atoms of the other metal may modify its electronic properties via electron removal/donation and thereby change its interaction with adsorbing species. Structural or geometric effects are important only for structure-sensitive reactions such as ethane hydrogenolysis which require a large ensemble of active metal atoms. Addition of a second metal may reduce the size of such an active ensemble and thus reducing the activity for that reaction. On the other hand, the second metal may form active ensembles of its own or may give rise to mixed ensembles.

A bimetallic catalyst is well characterized when we know whether bimetallic particles (or clusters) are actually formed and if they are formed, what is the surface composition of the bimetallic particles. It is also important to know whether the surface composition is uniform over all the clusters. The extent and uniformity of co-clustering in bimetallic catalysts depends on various factors such as the method of catalyst preparation and activation, type of
support, physical properties of the support, the nature of the catalyst precursors used as well as the nature and loadings of the metals in the catalyst (4).

Quantitative measurement of surface compositions is an important area of catalytic research which has not received the deserved attention. The surface compositions of bimetallic catalysts in the form of single crystals have been studied extensively (5-11) by using Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS). There are however, very few techniques available to determine the surface composition of supported bimetallic catalysts. One of the techniques is selective chemisorption. The problem is quite straightforward when Group VIII metals are combined with Group IB metals to form bimetallic clusters such as Ru-Ag or Ru-Au because it can be assumed that hydrogen does not adsorb on the Group IB metal. Supported bimetallic clusters formed between Group VIII metals such as Pt-Rh system studied here, represent a greater challenge because both metals usually adsorb most of the commonly used adsorbates such as hydrogen, carbon monoxide and oxygen. Miura et al. (12-15) have succeeded in measuring the surface compositions of a series of alumina and silica supported Pt-Ru bimetallic clusters using a selective titration technique. In this method, advantage was taken of the fact that the titration stoichiometry of the reaction between chemisorbed O₂ and gas phase CO is very different on Ru and Pt. However, it must be kept in mind while using such a technique that coadsorption of two species may result in surface reconstruction.
as well as in chemisorption induced surface segregation. Adsorbates are known to influence the surface compositions of bimetallic catalysts and the effect of one adsorbate on the surface composition of the bimetallic catalyst may or may not be reversible. Wang and Schmidt (16) observed that the surface of silica supported Pt-Rh catalysts was enriched in Rh by oxidation-reduction cycling. Miura and Gonzalez (14) have used IR spectroscopic method to determine the surface compositions of Pt-Ru/SiO₂ catalysts. Wu et al. (17) used ¹H NMR spectroscopy to determine the surface composition of supported bimetallic catalysts. Wang et al.(18) have used ¹³C NMR of adsorbed CO and ¹⁹⁵Pt NMR spectroscopy in order to characterize alumina supported Pt-Rh catalysts and found that the surfaces of their bimetallic catalysts were enriched in rhodium. Under reaction conditions, the surfaces of catalysts are covered with reactants and hence understanding the influence of various reactants on the surface composition of the bimetallic catalysts is important. The surface compositions of the alumina and silica supported Pt-Rh catalysts were determined in the presence of hydrogen by ¹H NMR which is described in Chapters 3 and 5, and in the absence of any adsorbate by ¹²⁹Xe NMR which is discussed in Appendix B.

Several hydrogenation reactions are carried out industrially on supported transition metal catalysts for treatment of petroleum feedstock. Further many hydrogenolysis reactions are used to gain fundamental understanding of catalytic surfaces. The mobility of hydrogen on catalytic surfaces may be
important in understanding the mechanisms of these reactions on such surfaces. As it dictates the coverage and availability of adsorbed hydrogen on the catalyst surface. Engelke et al. (19) found out that the interparticle motion of hydrogen on the surfaces of Ru/SiO₂ catalysts occurred via the gas phase and involved hydrogen adsorption-desorption processes. Hence understanding the various factors related to mobility of hydrogen and kinetics of adsorption-desorption on the surfaces of such supported catalysts is also important. The parameters related to the kinetics of adsorption and desorption processes are estimated by studying hydrogen mobility on the surfaces of these catalysts. A detailed study was done of the kinetic parameters for adsorption and desorption of hydrogen on silica supported Pt, Rh and Pt-Rh bimetallic catalysts and is described in Chapters 4 and 5. The differences in hydrogen mobility on Pt and Rh catalysts could explain the different activity exhibited by these two catalysts towards various reactions such as hydrogenolysis and isomerization.

As mentioned earlier, bimetallic catalysts consisting of Group VIII–Group IB metals are easier to characterize because hydrogen does not usually adsorb on Group IB metals and the total hydrogen uptake can be related to the fraction of Group VIII metal at the surface. The ruthenium-silver bimetallic system serves as a model system in understanding the catalytic behavior of more complicated systems involving ruthenium. The technique of ¹H NMR spectroscopy is quite suitable for this purpose because it is a quantitative technique and since silver
does not dissociatively adsorb hydrogen, the fraction of Ru atoms exposed at the surface can be directly and quantitatively determined. Further the electronic and geometric effects of Ag on Ru can also be studied by $^1$H NMR with the help of atomistic simulations (20). Since there is no added complication of hydrogen spillover (21) from Ru to Ag, the study of hydrogen mobility on these surfaces can also illustrate the effect of Ag addition on catalytic properties of Ru. Hence Ru-Ag/SiO$_2$ catalysts were studied by $^1$H NMR spectroscopy with an emphasis on the chemisorption and mobility characteristics of hydrogen on these surfaces and is described in Chapter 6. The modification of the properties of Ru by adding inactive group IB metals such as Ag may be complimentary to the modification of Ru surface by alkali metals such as potassium which is a more complicated system. It is known that potassium partitions itself between Ru metal particles and silica support (22). Thus potassium affects the chemisorption and mobility of hydrogen on the metal as well as the support. The promotional effects of potassium on Ru can be understood by studying the kinetics and energetics of hydrogen adsorption-desorption on such catalysts and based on the understanding of the simpler Ru-Ag bimetallic system. This is discussed in a separate paper in Appendix A.
Dissertation Organization

The dissertation consists of four papers (Chapters 3-6) followed by general conclusions. Each paper was written by the author in a form suitable for publication in a technical journal. The paper corresponding to Chapter 3 has been accepted in the Journal of Catalysis. The papers in Chapters 4, 5 and 6 will be submitted for publication with the author of this dissertation as the primary author. Chapters 3, 4 and 5 describe the original work carried out by the author. Chapter 6 also describes the original work done by the author along with the work on microcalorimetry done by R. L. Narayan. Appendix A describes the work done on potassium promoted Ru catalysts using $^1$H NMR and microcalorimetry. Appendix B details the work done on Pt-Rh/Al$_2$O$_3$ catalysts by $^{129}$Xe NMR spectroscopy. Appendix C describes the experimental estimation of gas phase hydrogen and compares it with calculations based on ideal gas law. Appendix D discusses the possible nature of adsorbed hydrogen labeled as $\alpha$ and $\beta$ hydrogen along with some relevant calculations. Appendix E describes the work on interaction of CO and H$_2$ on Ru/SiO$_2$ catalyst. References for the General Introduction, Literature Review and General Conclusions chapters are given at the end of the thesis, after Appendix E.
CHAPTER 2. LITERATURE REVIEW

Theory of surface segregation

The term surface segregation refers to the enrichment of one or more components of a mixture near the surface region, relative to the bulk. Chemical models of surface segregation are of two types: Macroscopic and Microscopic models. From macroscopic thermodynamic models, only a macroscopic picture of the surface, such as the average composition for a structurally uniform surface can be obtained whereas detailed, site-specific surface composition profile can be obtained from microscopic models. The macroscopic models require the input of macroscopic thermodynamic properties such as pure component surface tensions while microscopic models require detailed bond energy information. The macroscopic models are applicable to continuum surface only whereas the microscopic models can be applied to any surface.

Gibbs (23) showed that at equilibrium, the surface excess $\Gamma_A$, of component A in a binary alloy AB is given by,

$$\Gamma_A = -\frac{d\sigma}{d\mu_A} = \frac{(N_A^{\text{Tot}} - N_A^\alpha + N_A^\beta)}{S}$$ \[1\]

where $\mu_A$ is the chemical potential of component A and $\sigma$ is the surface free energy of the alloy. Further, $S$ is the interfacial area, $N_A^{\text{Tot}}$ is the total number of moles of A in the system and $N_A^\alpha$ and $N_A^\beta$ represent the number of moles of A in phase a
and b. (For a surface interfacing with vacuum, \( N_A^g = 0 \)). This expression indicates that if increased amount of component A in a binary alloy AB lowers the surface free energy of the alloy then surface segregation of A would occur. However, equation [1] can not be readily used to calculate surface compositions, given only overall compositions, temperature and pressure. Hence attempts were made to develop models of predicting surface segregation, that use easily measurable or obtainable data. One such model was developed by Butler and Schuchowitzky (24,25) based on the assumptions of monolayer surface region, ideal solution behavior and equal molar surface areas of constituents. This expression, which can be used to calculate the surface compositions in terms of measurable quantities, is as follows:

\[
X_{SA} / X_{SB} = (X_{A} / X_{B}) \exp [ S(\sigma_B - \sigma_A)/RT ] \quad [2]
\]

where \( X_{SA} \) and \( X_{SB} \) are the first layer (surface) mole fractions of A and B, \( X_{A} \) and \( X_{B} \) are the bulk fractions of A and B, \( \sigma_A \) and \( \sigma_B \) represent the pure component surface tension for A and B, \( S \) is the surface area and \( T \) is temperature in K. The effects of the surface tension of the components and of the temperature on the surface composition of the binary system can be easily seen from equation [2]. It predicts that the component with lower surface tension will be enriched at the surface and as the temperature is increased, the surface composition approaches the bulk composition. However, the ideal solution model assumes the heat of mixing of components of a binary alloy to be zero. Other models were developed
by Guggenheim (26) and later refined by Defay and Prigogine (27), based on regular solution theory which takes into account the effects of heat of mixing.

In the microscopic models, it is suggested that the energy of the system can be described by analyzing the bonds between the metal atoms. Since bonds between atoms in the bulk have to be broken in the creation of a surface, these models are sometimes referred to as broken bond models (4). Since it is energetically favorable to break the weakest bonds, it was predicted that the component of a binary alloy having the lower heat of sublimation (bulk cohesive energy), a measure of the bulk bond strength, should segregate to the surface. However, these earlier broken bond models were not accurate because they assumed bond energies to be invariant with coordination. Another less rigorous model is the elastic strain model (4) which proposes that significant elastic strain exists in the lattice when a solute atom is placed in a matrix of atoms of unlike size. If the solute is moved to the surface, the elastic strain energy is reduced. According to this model then, the solute would segregate to the surface of an alloy whenever it is either significantly smaller or larger than the matrix atom.

The input required for the microscopic models is usually detailed information on bond energies and a symmetric mixing model. With these models, it is possible to model flat as well as structured or stepped surfaces. We can obtain microscopic information such as surface composition at basal planes, defect sites (edges and corners) and distribution of ensemble sizes, from these models.
For Pt-Rh system, the bulk cohesive energy for Rh is 554 kJ/mole which is lower than that for Pt which is 563 kJ/mole. Thus based on bulk properties, Rh segregation to the surface would be predicted. The atomic radii of Pt and Rh are 1.39 and 1.34 Å, respectively and the surface segregation behavior of this system can not be predicted based on the elastic strain model. However, these models are not accurate because these do not take into account the surface energies of Pt and Rh which would dictate the surface segregation behavior of the system. The surface energy for (111) plane is 100 kJ/mole for Pt and 110 kJ/mole for Rh in case of 31% dispersed cluster. Hence based on surface energies, platinum segregation to the surface would be predicted which is found to be correct according to many theoretical and experimental studies (5-11).

Pt-Rh bimetallic system

Adsorbate-Free Pt-Rh Surfaces

The calculations done by van Delft et al. (3) using a Monte Carlo method predict that the surface composition is almost equal to the bulk composition. Schoeb et al. (28), based on atomistic simulations for adsorbate free Pt-Rh clusters, predicted surface enrichment of Pt at 973 K.

Beck et al. (9) studied Pt_{10}Rh_{90}(111) crystal face in vacuum (5x10^{-10} Torr) using ion scattering spectroscopy (ISS) and Auger electron spectroscopy (AES). They observed that the surface composition remained the same as the bulk composition up to 600°C, but the surface became enriched in Pt above 600°C.
Williams and Nelson (5) using ISS, observed that the surface composition was almost equal to the bulk composition at room temperature and surface was enriched with Pt at $T > 800$ K for disks of unsupported Pt-Rh catalysts. Similarly Pt enrichment of the (111) surface of Pt$_{0.1}$Rh$_{0.9}$ alloy was observed by Holloway and Williams (6) using AES at 1000 K and also by van Delft et al. (3) for (100) and (410) surfaces of Pt$_{0.25}$-Rh$_{0.75}$ alloy using AES. van Delft et al. (3) observed that Pt surface segregation increased with increasing equilibration temperature. van Langeveld and Niemantsverdriet (7) using AES observed Pt enrichment of the surface of a polycrystalline Pt-Rh alloy.

Impurity atoms may also influence the surface compositions of bimetallic catalysts. Ahmad and Tsong (29) using atom probe field ion microscopy (APFIM) found that the surface composition of Pt-Rh alloys was oscillatory in nature since the top layer of (001) plane of Pt-Rh alloys showed a significant enrichment of Rh and a considerable depletion of Rh in the second layer. The adsorbed sulfur was speculated to be the cause Rh to be enriched in surface.

**Adsorbate covered surfaces**

**Oxygen and NO**

The surface of Pt-Rh single crystals studied using AES, was found to be enriched in rhodium under the influence of oxygen, by Wolf et al. (30) and van Delft et al. (3, 8) in the temperature range of 600 to 1000 K. Williamson et al. (11) also observed by AES, the surface enrichment in Rh of Pt-Rh foils above 773 K in
the presence of oxygen. van Delft et al. (3) observed a similar effect for adsorbed NO on Pt-Rh alloys and this was attributed to the formation of oxygen adatoms upon NO dissociation.

Beck et al. (9, 10) have examined the surface composition of $\text{Pt}_{10}\text{Rh}_{90}(111)$ single crystal using ISS and AES. They also observed that the surface was enriched in rhodium in low pressure ($10^{-6}$ Torr, T: 800-1000°C) and high pressure (38 Torr, T: 500-600°C) oxygen environments. The authors further reported that on annealing this Rh enriched surface in the range 950-1000°C, the surface became enriched in Pt again indicating that oxidation of Rh was reversible by annealing in vacuum at high temperatures. Similarly, a reducing environment could also result in a reversal of surface composition.

Wang and Schmidt (16) studied 50-200 Å diameter particles of Pt-Rh alloys and pure metals deposited on planar amorphous silica by transmission electron microscopy (TEM) and found that surface of silica supported Pt-Rh alloys was enriched in Rh after oxidation-reduction cycling. Kacimi and Duprez (30) have measured the surface composition of Pt-Rh catalysts supported on alumina using $^{18}\text{O}/^{16}\text{O}$ isotopic exchange. They observed that catalysts which were annealed in oxygen at 700°C and 900°C, had surface composition different from the bulk composition. Below a critical bulk Rh composition $X^*$, the surfaces of the bimetallic catalysts were enriched in Pt and above $X^*$, those were enriched in Rh. The composition $X^*$ was dependent on the annealing temperature.
Hydrogen and CO

Beck et al. (9) noted that the surface became enriched in Pt, from 31% Pt to 38% Pt under $10^{-6}$ Torr H$_2$. Under high pressure (38 Torr) of hydrogen, they observed (10) that the surface composition increased to 31% Pt, starting with initial composition of 4% Pt, but remained constant at 31% Pt when initial composition was 31% Pt. van Delft et. al. (8) also found that CO and H$_2$ do not exert a significant influence on surface composition of Pt-Rh alloys. They did not find any evidence for CO dissociation.

Zhu and Schmidt (31) studied silica supported Pt, Rh and Pt-Rh alloy particles by CO chemisorption using temperature programmed desorption (TPD). These workers observed that oxygen treatment completely suppressed CO chemisorption on Rh due to formation of an inactive Rh oxide and CO being incapable of reducing the oxide. However, oxygen treatment did not inhibit CO chemisorption on Pt. Alloy particles were transformed entirely to Rh$_2$O$_3$ with no exposed Pt atoms under the presence of oxygen at high temperatures. Reduction of this oxide in H$_2$ produced a surface whose CO chemisorption properties appear to be those of Rh. There was no evidence of CO dissociation on the surface of Pt, Rh or their alloys.

Oh and Carpenter (32) studied Pt, Rh and Pt-Rh bimetallic catalysts by measuring the activity of these catalysts for the CO oxidation reaction. They noted that Pt was more active for strongly oxidizing conditions and Rh was more
active for net reducing conditions. They also noted some synergism between Pt and Rh in the bimetallic catalyst which was explained in terms of geometric as well as electronic effects.

Wang (33) used $^{13}$C NMR to characterize Pt-Rh bimetallic clusters with adsorbed CO and supported on $\eta$-Al$_2$O$_3$. The author has discussed two possible extreme situations for the electronic structure of Pt-Rh alloy surfaces: (i) Pt and Rh electronic wave functions maintained their local electronic structure. CO adsorbed on these (assumed to be linearly bonded) had different electronic structure for Pt and Rh, resulting in two peaks in NMR spectra with peak positions same as those on pure metal surfaces. Relative intensity of the peaks would change with surface composition of the bimetallic catalysts. (ii) Pt and Rh electronic wave functions were highly delocalized and collective behavior of electrons was important. So there should be single peak with same Knight shift in the spectra and the peak position would change with surface composition. The author could not resolve these two cases from $^{13}$CO NMR lineshapes alone because, owing to broad lines, linewidths were comparable to the difference in line positions on Pt and Rh. He used $^{13}$C-$^{195}$Pt SEDOR (spin echo double resonance) experiment as a technique to distinguish CO attached to Pt from that attached to Rh. The SEDOR experiment gave results which agree with the "delocalized picture". $^{13}$CO NMR lineshift was found to be independent of CO coverage which
also indicated that CO did not preferentially bond to one metal than to the other, which again supported the "delocalized picture" for Pt-Rh bimetallic clusters.

Since CO may bind more strongly to Rh than Pt, the author tried to investigate whether the Rh segregation was induced by CO, by doing a $^{195}$Pt NMR experiment. The essential features of $^{195}$Pt NMR are two peaks; a "bulk" peak and a "surface" peak. The author (33) found that the position of the Pt line due to surface Pt atoms was the same both on clean and CO covered bimetallic surface. This indicated that the Rh enrichment of the surface was not caused by adsorbed CO. He has attributed it to the oxidation-reduction pretreatment given to their catalysts.

Thus the general observation has been that oxygen induces segregation of Rh to the surface of Pt-Rh bimetallic catalysts. The adsorbates CO and H$_2$ have been found to have no effect on surface composition of the bimetallic catalysts.

**Ru-Ag bimetallic system**

The Ru-Ag bimetallic system serves as a model system to study the chemisorption and mobility behavior of hydrogen. Strohl and King (20) using atomistic simulations found that silver segregates to the surface of Ru-Ag bimetallics. Wu et al. (34) also found by $^1$H NMR that silver segregated to the surface of Ru-Ag/SiO$_2$ catalysts but to a lesser extent than copper in case of the Ru-Cu system. Based on atomistic simulations of the Ru-Ag system (20, 35), it is known that silver preferentially occupies the defect like edge and corner sites on
Ru surface and forms two dimensional islands at higher silver contents. This has been also supported by the recent experimental evidence of Schick et al. (36) based on various surface spectroscopic techniques. Based on data obtained by photoemission of adsorbed xenon (PAX) spectroscopy, they reported that silver preferentially decorated Ru step sites on a stepped Ru(10117) surface whereas silver showed a tendency to form two dimensional islands on a flat Ru(0001) surface. This was further supported by other methods such as angle resolved ultraviolet photoemission spectroscopy (ARUPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS).

Wu et al. (34) noted by ¹H NMR that silver does not interact with ruthenium as strongly as copper. Based on evidence from X-ray photoemission spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES), Rodriguez (37) found that silver does not exhibit any electronic interaction with Ag. Smale and King (35) also ruled out such an effect for Ru-Ag/SiO₂ catalysts. However Rodriguez (37) proposed that there are changes in the valence bands of Ru and Ag which result in increase in the strength of the Ag-CO bond and weakening in the Ru-CO bond. This was attributed to a decrease in π backdonation from Ru to CO in the presence of Ag. From temperature programmed desorption (TPD) data, he also observed that Ag adatoms block the adsorption of CO and O₂ on Ru(0001) on a one-to-one basis.
Bernasek and Somorjai (38) observed that the hydrogen-deuterium exchange reaction occurred mainly at the defect-like step sites and these defect-like sites are thought to be highly active for the dissociative hydrogen adsorption and associative hydrogen desorption processes. Smale and King (35) observed that the Ru-Ag/SiO₂ catalysts were less active for ethane hydrogenolysis than Ru/SiO₂ catalysts, at all temperatures. The activity for the reaction decreased with increasing silver content and became more or less constant at 30 atomic % silver. Since ethane hydrogenolysis involves dehydrogenated intermediate species, hydrogen removal from the surface was important because otherwise hydrogen would act as an inhibitor for the reaction. It was proposed by Smale and King (35) that the defect-like sites are active for hydrogen desorption from the surface and since silver blocked these sites, hydrogen desorption was prevented which resulted in lower activity for the reaction. Bhatia et al. (39) also used similar arguments to explain their ¹H NMR results on Ru/SiO₂ and Ru-Ag/SiO₂ catalysts. They observed two adsorbed states of hydrogen termed α and β, on the surfaces of these catalysts. They also observed that the population of a weakly bound species of hydrogen (termed as β resonance) was reduced by addition of silver. It was proposed that the beta hydrogen population depends on hydrogen adsorption and desorption at the defect-like sites. Since silver suppressed these processes by blocking the edge and corner sites, it reduced the population of the beta hydrogen.
CHAPTER 3. INFLUENCE OF HYDROGEN CHEMISORPTION ON THE SURFACE COMPOSITION OF Pt–Rh/Al₂O₃ CATALYSTS

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Abstract

The surface compositions of a series of platinum-rhodium bimetallic catalysts supported on g-alumina were determined in the presence of chemisorbed hydrogen by ¹H NMR spectroscopy. The surface compositions of hydrogen covered Pt-Rh bimetallic catalysts were found to be slightly enriched in Rh, significantly different from the surface compositions of adsorbate-free Pt-Rh surfaces which are enriched in Pt. Further, based on selective excitation NMR experiments it was found that bimetallic particles of fairly uniform compositions were formed. Atomistic simulations of hydrogen covered Pt–Rh bimetallic catalysts were done using a method which involved coordination
dependent bond energies. The simulations indicated that the heat of adsorption of hydrogen on rhodium is about 13 kJ/mole higher than that on platinum. Finally, a general, qualitative method to predict the influence of adsorbates on the surface segregation behavior of bimetallic systems is described based on the knowledge of the surface energies at various sites and the heats of adsorption.

Introduction

Supported bimetallic or multimetallic catalysts are commercially useful because they often exhibit improved activity, selectivity or stability compared to monometallic catalysts (1). For example, platinum–rhodium catalysts find applications in industrially important reactions such as oxidation of ammonia to nitric oxide, control of automobile exhaust emission and synthesis of hydrogen cyanide (2). In addition to their various applications, such catalysts offer opportunities to explore challenging scientific questions. In principle, one can vary the surface properties of these catalysts in a systematic manner simply by altering the overall metal composition (3-5). The composition of bimetallic catalysts is often significantly different at the surface compared to the bulk due to the differences in surface energies of the two metals. The surface composition or the relative fraction of the two metals at the surface is an important parameter in the study of catalytic phenomena. For example, the activity per metal site (turnover frequency) of reactions, which is needed to deduce the
reaction mechanisms from kinetic data and to understand controlling factors such as ensemble or electronic effects, is based on the surface composition of the catalytically active metal (1,6,7,8).

It is well known that adsorbates on bimetallic surfaces can alter the surface composition of such systems, and while various theoretical models (9-13) can predict the surface segregation behavior of a particular bimetallic system, the influence of adsorbates is difficult to quantify. In the case of platinum-rhodium bimetallic system both theory and experiment (13-16) suggest that platinum segregates to the surface of a clean Pt-Rh bimetallic. Although the bulk cohesive energy of Rh is slightly smaller than that of Pt, the surface energy of Rh is larger than that of Pt. However, the difference in the surface energies of Pt and Rh is small and this difference can be altered by an adsorbate, perhaps even resulting in a reversal of the surface segregation behavior of the Pt-Rh system. For example, in the presence of oxygen it was observed using Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS) that the surfaces of Pt–Rh single crystals were enriched in Rh (17-20).

The influence of hydrogen on the surface composition of Pt–Rh bimetallic system has been studied less extensively. Van Delft et al. (17,18) studied Pt–Rh single crystals in the presence of hydrogen and other adsorbates using AES and reported that hydrogen did not influence the alloy as much as $O_2$ and NO, but quantitative information about the influence of $H_2$ was not given. Beck et al.
(19, 20) using ISS and AES reported that the surface of a Pt$_{10}$Rh$_{90}$(111) single crystal became enriched in Pt under low pressure ($10^{-6}$ Torr) and high pressure (38 Torr) environments of hydrogen in the temperature range of 500–600°C.

A few studies of supported Pt–Rh catalysts using techniques such as transmission electron microscopy (TEM), isotopic exchange and nuclear magnetic resonance (NMR) spectroscopy have been pursued. Wang and Schmidt (21) using TEM reported that the surface of silica supported Pt–Rh catalysts became enriched in Rh by oxidation-reduction cycling. Wang et al. (23, 24) used $^{13}$C NMR of adsorbed CO and $^{195}$Pt NMR to study Pt-Rh bimetallic clusters supported on h-alumina. The surface was found to be slightly enriched in rhodium in the presence of adsorbed CO.

In this study, we report the use of $^1$H NMR spectroscopy to determine the surface compositions of γ-alumina supported Pt–Rh catalysts in the presence of hydrogen. This approach is based on a method employed earlier by Wu et al. (3) to determine the surface compositions of silica supported Ru-Cu bimetallic catalysts using $^1$H NMR Knight shifts. The experimental results are compared with atomistic simulations in order to estimate the difference in the energy of adsorption of hydrogen on the two metals.
Methods

Catalyst preparation

One platinum and one rhodium catalyst, each with a metal loading of 3 wt% and supported on γ-alumina (Johnson Matthey, BET surface area=100 m²/g) were prepared by incipient wetness impregnation method using H₂PtCl₆·6H₂O and Rh(NO₃)₃·2H₂O (AESAR) as precursors. Appropriate amounts of the metal salts were dissolved in distilled water and about 1 g of the alumina support per ml of water was added to the solution. The resulting slurry was dried at room temperature for 20 hours and then at 393 K for 8 hours. Three Pt–Rh bimetallic catalysts with metal loadings of 3% Pt – 1% Rh, 3% Pt – 3% Rh and 1% Pt – 3% Rh were prepared in a similar manner via co-impregnation.

All of the catalysts were reduced in flowing hydrogen at 673 K and subsequently washed with hot, deionized water to remove residual chloride and other soluble impurities. The final reduction was carried out at 673 K in the NMR probe for 2 hours, evacuating and replacing the hydrogen every 30 minutes. Selective hydrogen chemisorption was used to measure the dispersion of the monometallic as well as the bimetallic catalysts. The total adsorption isotherm and the isotherm for weakly bound hydrogen were measured at room temperature using hydrogen pressures in the range of 20 to 50 Torr and then extrapolated to zero pressure to obtain the amount of strongly bound hydrogen adsorbed on the catalysts. An equilibration time of 10 minutes was used at each
pressure and the catalysts were evacuated to $5 \times 10^{-6}$ Torr for 10 minutes before recording the adsorption isotherm for weakly bound hydrogen according to a method described by Uner et al. (25). The dispersions of the 3% Pt and 3% Rh catalysts were 38% and 51% respectively. The dispersions of 3% Pt - 1% Rh, 3% Pt - 3% Rh and 1% Pt - 3% Rh catalysts were 25%, 20% and 18% respectively.

**NMR experiments**

The NMR experiments employed a home-built spectrometer with a proton resonance frequency of 250 MHz. The measurements were done using a home-built *in situ* NMR probe connected to a vacuum/dosing manifold which allowed for an easy control of hydrogen pressure during the measurements. The reduced sample was cooled to 573 K, evacuated overnight and then cooled to 304 K. Hydrogen was then dosed onto the sample at 304 K and equilibrated for 10 minutes before recording the NMR spectra. All spectra were recorded with a dwell time of 5 μs, a repetition time of 0.5 s and the number of scans varying from 3600 to 7200. Selective excitation experiments were done using a DANTE (delays alternating with nutations for tailored excitation) pulse sequence consisting of 30 short pulses (26). A pulse separation of 10 μs was chosen, resulting in a total duration of the DANTE sequence of 300 μs and a corresponding spectral excitation width of $\approx 3.3$ kHz. The overall flip angle of the DANTE sequence was adjusted by varying the width of the short pulse while
the rf amplitude remained constant. Following the DANTE sequence, a final 90° pulse was applied followed by the detection of the free induction decay.

Simulations

Atomistic simulations employing coordination dependent bond energies were used to determine the surface compositions of bimetallic systems as a function of particle size, temperature, compositions and chemisorption energetics (9,13, 27). The energy of the bimetallic system is given by,

\[ E = \sum N_t^A \epsilon (A_i) + \sum N_t^B \epsilon (B_i) + N_{AB} (\omega/z) \]  

[1]

where \( \epsilon (A_i) \) and \( \epsilon (B_i) \) are the energies contributed by atoms A and B, respectively, to each of its nearest neighbor bonds with coordination i, \( N_t^A \) and \( N_t^B \) are the number of atoms of type A and B, respectively, in each site, \( N_{AB} \) is the number of A-B bonds in the system, \( \omega \) is the mixing or interchange energy between the unlike atoms, A and B, and \( z \) is the bulk coordination (\( z = 12 \) for fcc metals). The partial bond energies \( \epsilon (A_i) \) and \( \epsilon (B_i) \) are obtained either from the corrected effective medium theory or experimentally determined parameters (27). The surface energies at various surface sites for Pt and Rh can be calculated from these partial bond energies and are listed in Table 1 along with the interchange energy for the Pt–Rh system. In order to model chemisorption, a term corresponding to the difference between the energy of adsorption of the
adsorbate on the two metals is added to the above expression [1] for the total energy of the system. We define this difference $\Delta$ for the Pt–Rh system as,

$$\Delta = | \Delta H_{ads, \text{Rh}} | - | \Delta H_{ads, \text{Pt}} |$$

.....[2]

where $\Delta H_{ads, \text{Rh}}$ and $\Delta H_{ads, \text{Pt}}$ are the heats of adsorption of hydrogen on rhodium and platinum respectively. The values reported (28-30) for the heats of adsorption of hydrogen on Pt and Rh cover a wide range (see Table 2). Hence the simulations were pursued for a range of $\Delta$ values at 304 K and a value giving the best fit for experimental data was found.

**Results**

All the $^1\text{H}$ NMR spectra obtained in this work exhibit a peak close to 0 ppm (from TMS) which represents diamagnetic hydrogen in the support, mainly due to hydroxyl groups. The hydrogen interacting with the conduction electrons of the metal particles appears as a second peak and is located significantly upfield.

The spectra in Fig. 1 were obtained for the 3% Rh/Al$_2$O$_3$ catalyst. The upfield peak at $-135$ ppm in Fig. 1(a) corresponds to hydrogen adsorbed on metallic particles of rhodium at 7 Torr and the spectrum in Fig. 1(b) was obtained after subsequent evacuation of the catalyst for 10 minutes. These shifts are consistent with previous studies. Sheng and Gay (31) reported shifts in the range of $-140$ to $-170$ ppm for hydrogen coverages varying from 0.3 to 1.0
on a 50% dispersed Rh/SiO₂ catalyst. Sanz and Rojo (32) observed a Knight shift of -120 ppm on Rh/TiO₂ catalysts at 10 Torr H₂.

The spectra for the 3% Pt supported on deuterated Al₂O₃ are shown in Fig. 2. The hydrogen-on-platinum (H/Pt) resonance shift is less than that for rhodium and strongly overlaps with the resonance from hydrogen in the support [Fig. 3(a)]. In order to better resolve the H/Pt resonance, the support was subjected to deuterium exchange by heating to 673 K in 760 Torr of D₂ for 2 hours, with fresh D₂ gas introduced at intervals of 30 minutes. The sample was then evacuated to 10⁻⁶ Torr and cooled to room temperature. The ¹H NMR spectrum of the deuterated support [Fig. 2 (a)] indicated a greatly diminished proton intensity near 0 ppm. Subsequently, hydrogen gas was introduced at an equilibrium pressure of 7 Torr [Fig. 2(b)]. Hydrogen adsorbed on Pt is represented by the difference of these two spectra [Fig. 2(c)] and exhibits a relatively narrow peak at -16 ppm. This result is consistent with earlier work by Sheng and Gay (31, 33) who reported ¹H NMR shifts in the range of -50 to -20 ppm for Pt particles with hydrogen coverage varying from 0.2 to 1.0 on a Pt/SiO₂ catalyst with a dispersion of 30% and of about -10 ppm for Pt particles with hydrogen coverage of 1.0 on a 40% dispersed Pt/Al₂O₃ catalyst.

The results for the monometallic Pt and Rh catalysts are compared with the bimetallic Pt-Rh catalysts in Fig. 3. All spectra were taken after exposure to hydrogen at 7 Torr for about 10 minutes and show an increasing upfield shift of
the hydrogen-on-metal resonance with increasing Rh content. The values of Knight shifts for hydrogen interacting with metallic particles in these spectra are given in Table 3.

The spectra in Fig. 4 (a) and (b) correspond to the 1% Pt – 3% Rh/Al₂O₃ catalyst at 7 Torr H₂ and 10⁻⁵ Torr H₂ (after 10 minute evacuation), respectively. The result of the selective excitation (DANTE) experiment with the 1% Pt – 3% Rh catalyst is given in Fig. 5. It can be seen that the H/Pt–Rh resonance line was saturated at a pressure of 7 Torr [Fig. 5(a)]. However, selective inversion of the population in the frequency band corresponding to the pulse sequence applied could be achieved at 10⁻⁵ Torr [Fig. 5(b)]. The purpose of the selective excitation experiment was to verify the formation of bimetallic particles (explained in detail in the next section).

Discussion

It is first noted that only one upfield peak is observed in the spectra for all catalysts that were exposed to 7 Torr of hydrogen (see Fig. 3). Further, the hydrogen-on-metal peak shifts toward upfield as the Rh content increases. These observations allow us to utilize ¹H NMR as a probe of the composition of bimetallic particles. To validate this method, we briefly summarize some of our earlier investigations of the dynamics of hydrogen on the surfaces of supported metals. In a study of hydrogen adsorbed on silica-supported ruthenium, Engelke
et al. (26) showed via selective excitation using the DANTE sequence that at low hydrogen pressures (e.g., $10^{-4}$ Torr) the hydrogen-on-metal NMR line is inhomogeneously broadened. It was also shown that the distribution of resonance frequencies resulted from differences in Knight shifts on particles of various sizes and shapes, and not from heterogeneity of individual adsorption sites. Furthermore, at low pressures, the hydrogen may undergo a quasi three-dimensional motion around the metal particles without desorbing from the surface. When the hydrogen pressure was increased to about 0.5 Torr, a transition from inhomogeneous to homogeneous line broadening occurred. A detailed analysis of lineshapes and the activation energies involved showed that this transition was a result of hydrogen motion that involved several processes: fast diffusion on a single particle, recombination, desorption, interparticle diffusion and readsorption (26). A similar effect was observed when the selective excitation experiment was performed with the catalysts studied in this work: at a low hydrogen pressure of $10^{-5}$ Torr the line was inhomogeneously broadened, but a transition to homogeneous broadening occurred at elevated pressures. An example of such transition is shown in Fig. 5 for a 1%Pt–3%Rh/Al₂O₃ catalyst. Thus, at a pressure of 7 Torr, hydrogen is in fast exchange with all surface metal sites present in the sample as it moves from one metal particle to another, whereas at $10^{-5}$ Torr the interparticle motion is restricted. Clearly, if monometallic Pt and Rh particles were present in large concentrations then two
separate resonances corresponding to H/Pt and H/Rh would be visible at these lower pressures. Instead, only one resonance was observed at $10^{-5}$ Torr which has a slightly increased linewidth and almost the same position compared to the resonance at 7 Torr (Fig. 4). This result suggests that for the most part bimetallic particles are formed and the concentration of monometallic particles is negligible. In addition, since the resonance at $10^{-5}$ Torr does not cover a broad range of resonances between H/Pt (−16 ppm) and H/Rh (−135 ppm), we can infer that the distribution of particle compositions is fairly narrow.

The interpretation of the observed shifts in terms of surface composition is not straightforward. It is generally recognized that the large $^1$H Knight shifts occur because of the bonding overlap between the hydrogen 1s orbitals and the conduction electrons of the underlying metals. Although the local density of electronic states on the surface of a bimetallic particle must reflect the surface segregation, it is not apparent at what range Pt and Rh retain their own electronic character. Two limiting cases can be considered: (I) a localized model which would result in the hydrogen shift on Pt and Rh to be independent of other neighboring and underlying atoms and identical to that on pure metals, and (II) a non-local picture which assumes that the adsorbed hydrogen experiences an average environment dependent on the sample composition. These two cases are discussed below in more detail.
According to the localized model, in the absence of motion we should observe two resonance shifts $\delta_{\text{Pt}}$ and $\delta_{\text{Rh}}$ consistent with hydrogen on pure Pt and Rh. The presence of one hydrogen-on metal resonance suggests that hydrogen is in fast exchange on Pt and Rh adsorption sites relative to the NMR time scale. The correlation time $\tau_{\text{ex}}$, for this dynamic exchange process must satisfy the condition $\tau_{\text{ex}}<\left(\frac{2\pi\Delta\nu}{A}\right)^{-1}$, where $\Delta\nu$ is the difference between the resonance frequencies of the exchanging spins. In this exchange process an adsorbed proton experiences a Knight shift interaction that is proportional to the hyperfine field contributed from Pt and Rh sites in the lattice (34) and the observed shift, $\delta_{\text{Pt-Rh}}$, can be expressed by the following:

$$\delta_{\text{Pt-Rh}} = \delta_{\text{Pt}} X^S_{\text{Pt}} + \delta_{\text{Rh}} X^S_{\text{Rh}}$$

where $X^S_{\text{Pt}}$ and $X^S_{\text{Rh}}$ are the surface atomic fractions of Pt and Rh, respectively. The above expression can be used to determine the surface compositions of Pt-Rh/Al$_2$O$_3$ catalysts from the monometallic shifts, $\delta_{\text{Pt}}$ and $\delta_{\text{Rh}}$, from Figures 3(a) and 3(e), respectively. This procedure is based on two further assumptions:

(i) The hydrogen to metal stoichiometry at the surface is the same for both metals. This assumption appears to be well justified by the results of $^1$H NMR spin counting. The integrated intensities of hydrogen-on-metal peaks in the $^1$H NMR spectra at 7 Torr of hydrogen yielded approximately the same $H/Pt_{\text{surface}}$ and $H/Rh_{\text{surface}}$ ratios [1.2 ($\pm$ 0.2) and 1.1 ($\pm$ 0.2), respectively] for the Pt/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts.
(ii) The shifts $\delta_{\text{Pt}}$ and $\delta_{\text{Rh}}$ are both independent of particle size. This is justified simply by noting that the distribution of shifts for Pt/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ is small compared to the difference between the resonance line positions for these two catalysts.

(II) The segregation of atoms on the surface of highly disordered bimetallic systems has been successfully described by the tight-binding Hartree-Hamiltonian model to determine the electronic energy (35). According to this model, the local electronic density of states $\rho_\lambda(E)$ of the bimetallic system can be described in terms of the densities of states of individual components (Pt and Rh in our case) as:

$$\rho_\lambda(E) = \rho_{\lambda,\text{Pt}} X_{\lambda,\text{Pt}} + \rho_{\lambda,\text{Rh}} (1 - X_{\lambda,\text{Pt}}) \quad \text{[4]}$$

The above relationship is valid for the bulk as well as for surface layers (subscript $\lambda$ denotes the coefficients for the $\lambda$th layer). On the other hand, the Knight shift is dominated by the Fermi contact term which can be expressed as $K=<a>\chi_p$, where $<a>$ denotes the hyperfine coupling constant and $\chi_p$ is the Pauli susceptibility. Since Pauli susceptibility is directly proportional to the density of states at the Fermi surface, the Knight shift for a disordered system can be also expressed by an equation similar to [4]. Thus, regardless of hydrogen dynamics and without the assumptions (i) and (ii) discussed earlier for the localized case, the NMR shifts can be used to determine a 'non-local' concentration $X_{\text{Pt}}$. 

Although it is unclear how many underlying layers affect the adsorbed atom, the data presented here indicate slight rhodium segregation (as discussed later) in the region of the particle that is probed by $^1$H NMR. The non-local model has been earlier postulated for similar Pt-Rh bimetallic clusters based on $^{13}$C NMR studies of adsorbed CO (23, 24).

We finally note that regardless of which model is operable in the system under study, NMR provides us with a unique and valid insight because it probes the very properties of the metal surface that are responsible for their catalytic performance, at least in reactions determined by the adsorption characteristics of hydrogen. The influence of hydrogen on the surface compositions of Pt-Rh catalysts, as observed in this work, is discussed below.

The experimentally determined and simulated values of surface rhodium composition (expressed as atom fraction) are plotted against the overall rhodium composition in Fig. 6. The simulations were performed at 304 K with the parameter $\Delta$ fitted to give the best agreement with the surface compositions derived from NMR. The difference in the heats of adsorption of hydrogen on Rh relative to Pt was found to be 13 kJ/mole at 304 K. The simulations pursued at 673 K (not shown), the reduction temperature which is the highest temperature possible for equilibration of compositions, yielded a value of 15 kJ/mole for $\Delta$ indicating that this parameter is relatively insensitive to temperature.
The results presented in Fig. 6 clearly demonstrate the influence of adsorbates on the surface composition of a bimetallic catalyst. In the case of the adsorbate-free Pt-Rh system, the difference in the surface energies between the two metals determined from the site energies (see Table 1) for a 31% dispersed particle is about 10 kJ/mole favoring Pt on the surface. In the presence of hydrogen, it is seen from experimental results and theory that the surface is slightly enriched in Rh with the heat of adsorption of hydrogen about 13 kJ/mole greater on Rh than on Pt.

The above qualitative analysis is a useful, general procedure to assess the potential for an adsorbate in a reactive environment to influence the surface composition of a bimetallic catalyst. An example where the surface composition is not influenced by hydrogen chemisorption is the Ru-Cu bimetallic system. The difference in surface energies between Ru and Cu for a closed packed surface as estimated from site energies is about 80 kJ/mole. The heats of adsorption of hydrogen on Ru and Cu are roughly 90 and 40 kJ/mole, respectively, and the corresponding difference of 50 kJ/mole is significantly smaller than the difference in the surface energies. Thus hydrogen can not cause reversal of surface segregation behavior of the Ru-Cu bimetallic system and we would expect segregation of Cu to the surface of Ru-Cu bimetallic catalysts even in the presence of hydrogen. Indeed, Wu et al. (3), using $^1$H NMR,
observed that copper segregated strongly to the surface of hydrogen covered Ru-Cu/SiO₂ catalysts.

Conclusions

The surface compositions of Pt-Rh/Al₂O₃ catalysts in the presence of hydrogen were significantly different from those of adsorbate-free surfaces. The surface compositions determined via ¹H NMR indicated that the surface was slightly enriched in Rh as opposed to enriched in Pt on an adsorbate-free surface. Furthermore, selective excitation NMR of adsorbed hydrogen indicated that these Pt–Rh catalysts consisted primarily of bimetallic particles with a fairly narrow distribution of compositions.

A comparison of experimentally obtained surface compositions with simulated values gave an estimate of 13 kJ/mole for the difference between the heats of adsorption of hydrogen on Pt and Rh at 304 K with the heat of adsorption being higher on Rh. The approach given here can be generalized to predict the surface segregation behavior of a bimetallic system in the presence of various adsorbates if the overall difference between the metal surface energies and heats of adsorption of an adsorbate on the two metals are known. Such a method is very useful in predicting whether only one metal or both metals are present with significant concentration at the surface of bimetallic catalysts under reaction conditions. In this work, it was noted that both Pt and Rh were
present in significant concentrations at the surface of Pt-Rh bimetallic catalysts under the influence of hydrogen adsorption. Quantification of surface compositions under reaction conditions gives useful information which is required to determine the catalytic activity per active metal site (turnover frequency). A better understanding of the catalytic activity of bimetallic systems can be gained if these results are correlated with reaction studies.

Acknowledgments

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References


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Table 1

Surface energies (in kJ/mole) at specific surface sites (27)

<table>
<thead>
<tr>
<th>Site Type</th>
<th>Formula for site energy E</th>
<th>Surface fraction of site</th>
<th>$E_{\text{Rh}}$</th>
<th>$E_{\text{Pt}}$</th>
<th>$E_{\text{Rh}} - E_{\text{Pt}}$</th>
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<tbody>
<tr>
<td>Bulk</td>
<td>$12\varepsilon_{12}$</td>
<td></td>
<td>-554.55</td>
<td>-563.23</td>
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<td>(111) plane</td>
<td>$9\varepsilon_{9} - 12\varepsilon_{12}$</td>
<td>0.65</td>
<td>110.91</td>
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<td>(100) plane</td>
<td>$8\varepsilon_{8} - 12\varepsilon_{12}$</td>
<td>0.13</td>
<td>148.52</td>
<td>139.84</td>
<td>8.68</td>
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<tr>
<td>Edge</td>
<td>$7\varepsilon_{7} - 12\varepsilon_{12}$</td>
<td>0.19</td>
<td>186.14</td>
<td>178.42</td>
<td>7.72</td>
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<tr>
<td>Corner</td>
<td>$6\varepsilon_{6} - 12\varepsilon_{12}$</td>
<td>0.03</td>
<td>224.71</td>
<td>217.96</td>
<td>6.75</td>
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Mixing energy for Pt–Rh system = $-0.67$ kJ/mole
Table 2
Heats of adsorption of hydrogen on Pt and Rh in various forms

<table>
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<tr>
<th>Metal</th>
<th>Form</th>
<th>Temperature Range (K)</th>
<th>$\Delta H_{\text{ads, H}_2}$ (kJ/mole)</th>
<th>Ref.</th>
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<td>Pt</td>
<td>Film</td>
<td>278-395</td>
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<td>Foil</td>
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<td></td>
<td>Tip</td>
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<td>62.0</td>
<td>30</td>
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<td>Tip</td>
<td>80-300</td>
<td>105.2</td>
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<td></td>
<td>Supported:</td>
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<tr>
<td></td>
<td>(i) Charcoal</td>
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<tr>
<td></td>
<td>(ii) $\eta$-Al$_2$O$_3$</td>
<td>723</td>
<td>49.0</td>
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<td>(iii) SiO$_2$-Al$_2$O$_3$</td>
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<td>46.0</td>
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<td>(iv) SiO$_2$</td>
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<td>Filament</td>
<td>196-350</td>
<td>79.4</td>
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Table 3

$^1$H NMR results of hydrogen chemisorbed on $\gamma$-Al$_2$O$_3$ supported catalysts

<table>
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<tr>
<th>Catalyst</th>
<th>Knight Shift $\delta$ (ppm)</th>
<th>Overall Atom Fraction, $X^O_{Rh}$</th>
<th>Surface Atom Fraction, $X^S_{Rh}$</th>
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<tbody>
<tr>
<td>3% Pt</td>
<td>-16.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>3% Pt - 1% Rh</td>
<td>-74.0</td>
<td>0.39</td>
<td>0.49</td>
</tr>
<tr>
<td>3% Pt - 3% Rh</td>
<td>-110.0</td>
<td>0.66</td>
<td>0.79</td>
</tr>
<tr>
<td>1% Pt - 3% Rh</td>
<td>-123.0</td>
<td>0.85</td>
<td>0.90</td>
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<tr>
<td>3% Rh</td>
<td>-135.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Errors in Knight shifts: ± 1 ppm
Figure Captions

Figure 1. $^1$H NMR spectra for 3% Rh / $\gamma$-Al$_2$O$_3$ catalyst with (a) 7 Torr H$_2$ and (b) $10^{-5}$ Torr H$_2$ after evacuation of H$_2$ in (a) for 10 minutes.

Figure 2. $^1$H NMR spectra for 3% Pt / Al$_2$O$_3$ catalyst with sample with deuterium exchanged with support hydrogen at 397°C for 2 hrs, (a) evacuated to $5 \times 10^{-6}$ Torr, (b) same sample in (a) with 7 Torr H$_2$, (c) difference spectrum of (b)−(a).

Figure 3. $^1$H NMR spectra of hydrogen chemisorbed on the monometallic Pt and Rh and three bimetallic Pt-Rh catalysts supported on $\gamma$-Al$_2$O$_3$ with 7 Torr of hydrogen. (a) 3% Pt (b) 3% Pt−1% Rh (c) 3% Pt−3% Rh (d) 1% Pt−3% Rh and (e) 3% Rh. The overall mole fraction of rhodium − $X^0_{\text{Rh}}$ is indicated for each catalyst.

Figure 4. $^1$H NMR spectra for 1% Pt−3% Rh / Al$_2$O$_3$ catalyst with (a) 7 Torr H$_2$ and (b) $10^{-5}$ Torr H$_2$ after evacuation of H$_2$ in (a) for 10 minutes.

Figure 5. $^1$H NMR selective excitation experiments for 1% Pt−3% Rh / Al$_2$O$_3$ catalyst with (a) 7 Torr H$_2$ and (b) $10^{-5}$ Torr H$_2$.

Figure 6. Surface mole fraction of Rh against overall mole fraction of Rh for experimental data and atomistic simulations at 304 K in the presence and absence of hydrogen. The legend gives the values of $\Delta$ in kJ/mole,
corresponding to the difference between the heats of adsorption of hydrogen on platinum and rhodium.
Figure 1.

(a) 7 Torr H₂

(b) $10^{-5}$ Torr H₂

Shift (ppm)
Figure 2.
Figure 3.

7 Torr H₂

(a) 0.0
(b) 0.39
(c) 0.65
(d) 0.85
(e) 1.0

Intensity

Shift (ppm)
Figure 4.
Figure 5.

(a) 7 Torr H₂

(b) $10^{-5}$ Torr H₂
Figure 6.

Overall atomic fraction of Rh, $X_{Rh}^o$ vs. Surface atomic fraction of Rh, $X_{Rh}$.

- Dotted line: 13 kJ/mole
- Dashed line: 0 kJ/mole
- Squares: $^1$H NMR
CHAPTER 4. KINETICS OF HYDROGEN CHEMISORPTION ON SILICA SUPPORTED Pt, Rh AND Ru CATALYSTS

A paper to be submitted to Surface Science

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Abstract

The kinetics of hydrogen chemisorption on the surfaces of silica supported Pt, Rh and Ru catalysts was studied by means of \(^1\)H NMR selective excitation experiments. The values of the desorption and adsorption rate constants determined from the exchange parameter were higher on Rh and Ru catalysts as compared to the Pt catalyst. The differences in the values of the desorption rate constants were not only due to different activation energies of desorption on these metal surfaces but also due to significantly different pre-exponential factors. The apparent sticking coefficients of hydrogen were at least 10 fold lower on Pt as compared to Rh and Ru catalysts, causing lower rates of hydrogen adsorption on Pt catalysts as compared to Rh and Ru catalysts. However, the sticking coefficients of hydrogen on these supported catalysts were
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higher than those on corresponding single crystal surfaces at given temperature and hydrogen coverage. This suggested that the surface defects are active for the trapping and dissociation of H₂ molecules on the metal surfaces.

1. Introduction

Hydrogen is an important reactant for catalytic studies of practical as well as fundamental interest. Many commercial processes such as hydrocracking and hydrotreating of petroleum feedstocks involve hydrogenations over supported catalysts (1). Model reactions such as hydrogenolysis and isomerization are used for the purposes of fundamental studies. Valuable information regarding structure sensitivity or insensitivity of catalysts can be obtained by studying such reactions (2,3) and hydrogen plays an important role in these reactions. Hydrogen, adsorbed in various forms, is known to be highly mobile even at room temperature on the surfaces of transition metal catalysts (4,5). The availability and hence the mobility of hydrogen on the surfaces of transition metal catalysts may be important in understanding the mechanisms of such reactions (6, 7).

There is a wealth of experimental data regarding the hydrogen binding energy and sticking coefficients of hydrogen on various transition metal surfaces. Most of this data is obtained from techniques such as thermal desorption, work function measurements and molecular beam techniques. Goodman et al. (8) have studied binding energies and kinetics of adsorption-desorption of hydrogen
on Ru(1120) surface. Shimizu et al. (9) have reported a value of 0.25 for initial sticking coefficient $S_0$ of hydrogen on Ru(0001) whereas a $S_0$ value of 1.0 has been reported on Ru(1010) surface (10). The value of $S_0$ has been reported to be about 0.55 to 0.65 on Rh(111) surface at 150 K (11, 12) whereas it is about 1.0 on Rh(110) surface at 85 K (13). The value of $S_0$ for hydrogen has been reported (11, 14) in the range of 0.016 to 0.07 for Pt(111) and Pt(100) surfaces which are more “close packed” surfaces. The more “open” surfaces with lower Pt coordination, such as Pt(211) and Pt(110) have much higher values of initial sticking coefficients (14). Similarly, polycrystalline Pt filaments have higher hydrogen sticking coefficients (15, 16, 17 and see Table 3). This suggests that sticking coefficient is higher for the surfaces with defects or the presence of low coordination sites. It has also been reported that the hydrogen sticking coefficients decrease with temperature on Pt filaments (15). Although the interaction of hydrogen with single crystal transition metal surfaces has been studied quite extensively, no study reporting the kinetics of hydrogen chemisorption on supported metal catalysts, has come to our attention.

In this work, the dynamics of hydrogen on the surfaces of Pt, Rh and Ru catalysts supported on silica was studied using $^1H$ NMR selective excitation experiments. Using a multisite exchange model of Engelke et al. (4), values of the activation energy for hydrogen desorption, the rate constants of hydrogen
desorption and adsorption as well as sticking coefficients of hydrogen on Pt and Rh surfaces were obtained.

2. Methods

2.1. Catalyst preparation

Platinum, rhodium and ruthenium catalysts supported on silica were prepared by incipient wetness impregnation method using Pt(NH$_3$)$_4$(NO$_3$)$_2$ (AESAR) and Rh(NO$_3$)$_3$×2H$_2$O (AESAR) and Ru(NO)(NO$_3$)$_3$ (AESAR) as precursors. Appropriate amounts of the metal salts were dissolved in deionized water and a measured amount of support was added to the solution. The resulting slurry was dried at room temperature for 20 hours and then at 393 K for 8 hours.

All of the catalysts were reduced in flowing hydrogen at 673 K and subsequently washed with hot deionized water to remove residual water soluble impurities and reduced again in the NMR probe. Selective hydrogen chemisorption was used to measure the dispersion of the catalysts according to a method developed by Uner et al. (18) and these dispersions are listed in Table 1.

2.2. NMR Experiments

The NMR experiments were carried out using a home built spectrometer with a proton resonance frequency of 250 MHz. The measurements were done using a
home-built *in situ* NMR probe connected to a vacuum/dosing manifold which allowed for an easy control of hydrogen pressure during the measurements. All spectra were recorded at a temperature of 304 ± 1K. A dwell time of 5 μs was used and number of scans varied from 3600 to 7200 with a repetition time of 0.5 s for the NMR spectra. Selective excitation experiments were done using a DANTE pulse sequence consisting of 30 short pulses (4). A pulse separation of 10 μs was chosen resulting in total duration of 300 μs for the DANTE sequence and a hole width of 3.3 kHz. After a recovery period of 10 μs, a final 90° pulse was applied followed by the detection of the free induction decay.

The effect of motion on the frequency-selective inversion of spin magnetization was incorporated into a multisite exchange model by Engelke et al. (4). The model assumed that exchange occurs between all magnetically inequivalent sites and the magnetization exchange was treated as a first-order process. The "real" motional process for hydrogen motion was modeled as a second-order process with pseudo first-order rate constants introduced in the equations. The exchange process was characterized by the NMR exchange parameter $k_{ex}$ which quantified the average hydrogen mobility. It was shown that the exchange of hydrogen spins between different metal sites involved desorption from one site, gas phase diffusion and readsorption on another site. It was further shown that the exchange parameter $k_{ex}$ is related to the desorption rate constant $k_d$ by the relation,
\[ k_{ex} = \sum_{i=1}^{n} \sigma_i' k_{di} \] ....[1]

where \( \sigma_i' = \frac{(1 - \nu_i)\sigma_i}{(N-1)} \) with \( \nu_i = \frac{k_{ai}s_i^2}{\sum_{i=1}^{n} k_{ai}s_i^2} \) ....[2]

where \( s_i \) and \( k_{ai} \) correspond to the fraction of vacant sites and adsorption rate constant for site \( i \), respectively. Assuming that all the parameters, i.e., the adsorption and desorption rate constants as well as the hydrogen coverage and the fraction of vacant sites is uniform over the entire metal surface, the above equations can be simplified to, \( \nu_i = 1/N \) and hence \( \sigma_i' = \sigma_i / N \). In that case, the relationship between \( k_{ex} \) and \( k_d \) simplifies to

\[ k_{ex} = k_d \theta_H \] ....[3]

where \( \theta_H \) which is same as \( \sigma_i \) corresponds to the amount of hydrogen adsorbed per surface metal site \((H/M_{surface})\) or the surface coverage of hydrogen.

The desorption rate constant is related to the adsorption rate constant by the relation arising from adsorption-desorption equilibrium for hydrogen,

\[ k_a P_{H_2} (1 - \theta_H)^2 = k_d \theta_H^2 \] ....[4]

Thus the desorption and adsorption rate constants were determined upon knowing the exchange parameter. Once these coefficients were known, the apparent sticking coefficient \( S \) at that coverage and temperature was determined from the following relations:
\[ S = \frac{dN_a}{dN_f} \quad \text{......[5]} \]

\[ \frac{dN_a}{dt} = N_s \frac{d\theta}{dt} = N_s \left\{ k_a P_{H_2} (1 - \theta_{H_2}^2) \right\} \quad \text{......[6]} \]

\[ \frac{dN_f}{dt} = \frac{P_{H_2} A}{\sqrt{2\pi m k T}} \quad \text{......[7]} \]

where A is the surface area of catalyst sample, m is the mass of impinging gas particle, T is the surface temperature in K and \( N_s \) is the number of surface metal atoms which can be calculated knowing the weight of the sample and the catalyst dispersion. The quantities \( dN_a/dt \) and \( dN_f/dt \) represent the rates of hydrogen adsorption and impingement of hydrogen on catalyst surface, respectively. The apparent sticking coefficient refers to the entire surface of the metal particles although hydrogen adsorption might be occurring mainly on the defect-like sites. The sticking coefficient at a given temperature and hydrogen coverage was found to decrease in the order Rh>Ru>Pt.

3. Results and Discussion

The experimental selective excitation spectra for the Rh catalyst at various temperatures and a coverage \( (H/Rh) \) of 0.4 are compared in Fig. 1 with the simulated spectra obtained from the multi-site exchange model developed by Engelke et al. (4). The desorption and adsorption rate constants as well as the
sticking coefficients were obtained from the exchange parameter according to the procedure described in the methods section.

The selective excitation experiments were carried out at different temperatures and the exchange parameters and hence the desorption constants were obtained as a function of temperature. An Arrhenius plot is obtained from this data for Pt, Rh and Ru/SiO₂ catalysts (see Fig. 2). The activation energy \( E_{\text{des}} \) for hydrogen desorption was obtained from such a plot for all the catalysts. It can be seen that \( k_a \), \( k_d \) and \( S \) are much higher for Rh and Ru catalysts than those for Pt catalyst. The activation energy \( E_{\text{des}} \) for hydrogen desorption decreases in the order Rh>Pt>Ru. All these parameters, i.e., the desorption and adsorption rate constants, the apparent sticking coefficients and the activation energies of hydrogen desorption are listed in Table 1 for Pt, Rh and Ru/SiO₂ catalysts.

The sticking coefficients obtained in this work on silica supported Pt, Rh and Ru catalysts are plotted in Fig. 3. These were obtained as a function of coverage only on the Ru/SiO₂ catalyst at 296 K. The single crystal data on these metal surfaces is also plotted on this same graph for comparison (9-17). The sticking coefficients on the supported metal catalysts were observed to be higher than those on single crystal surfaces.
3.1. Sticking coefficients

As seen from Table 3, the closed, packed transition metal surfaces have lower hydrogen sticking coefficients than the crystallographically more "open" surfaces. Hence supported metal catalysts would be expected to exhibit higher sticking coefficients of hydrogen. This appears to agree with our results on Ru/SiO₂, Rh/SiO₂ and Pt/SiO₂ (see Fig. 3). The sticking coefficients of hydrogen on our Rh and Pt catalysts were found to be 0.52 and 0.014, respectively at hydrogen coverage of 0.4 and at 333 K and about 0.18 on Ru catalyst at 296 K an hydrogen coverage of 0.4. The sticking coefficients on Ru/SiO₂ were also determined as a function of coverage and are higher than the values reported on Ru(0001) surface (9). It was shown by Christmann et al. (19) and Rendulic et al. (20) that the concentration of surface defects governs the trapping and subsequent dissociation of a H₂ molecule. The roughness of crystallographically more "open" surfaces provides very efficient channels for trapping and subsequent dissociation. Since supported metal particles have much larger concentration of surface defects, it is reasonable that higher sticking coefficients of hydrogen were observed on supported metal catalysts in this work as compared to single crystal surfaces.

For most of the single crystal and even polycrystalline Pt surfaces, the sticking coefficient is almost zero at hydrogen coverage of 0.4. The sticking coefficient of hydrogen on Rh(111) at a coverage of 0.4 is much lower than that
on Rh/SiO₂ (obtained in this work) at the same coverage. However, the sticking coefficient on Rh(110) appears to be much higher but that is because the single crystal data was taken at a much lower temperature of 88 K as opposed to our data taken at 333 K. From the data on Pt filaments (see Table 2), it can be seen that the hydrogen sticking coefficient decreases with increasing temperature. If the adsorption occurs via a precursor mediated process then the sticking coefficient is determined by the number of jumps/hops of the adatoms on the surface before it can desorb (21). As the temperature is increased, the number of jumps increases almost exponentially and probability of desorption greatly increases resulting in lower sticking probability. Many workers (11, 14, 15) have reported that the shape/nature of the plot of the sticking coefficient versus hydrogen coverage on single crystal Pt and Rh surfaces suggests that adsorption is occurring via a precursor intermediate on these surfaces. In most of these studies two adsorbed states of hydrogen were observed from thermal desorption studies, one strongly bound state with high binding energy and the other with low binding energy ascribed to a precursor state. Norton and Richards (15) argue that the initial, high and constant values of the sticking coefficient are due to high probability of the precursor state translating into the more strongly bound state and S decreases rapidly with increasing θ because the probability of hydrogen in the precursor state translating into the more strongly bound state diminishes rapidly.
3.2. Activation energies of desorption

The adsorption and desorption rate constants were lower on Pt catalyst by a factor of 20 to 40 as compared to those on Rh and Ru catalysts at various temperatures and given hydrogen coverage.

Hydrogen desorption from transition metal surfaces is a second order, activated process and the desorption rate constant can be expressed as:

$$k_d = k_{d0} \exp \left( -\frac{E_{des}}{RT} \right),$$

where $E_{des}$ is the activation energy of desorption and $k_{d0}$ is the pre-exponential factor. The activation energies of hydrogen desorption on Rh, Pt and Ru surfaces were found to be 79, 66 and 43 kJ/mole at a hydrogen coverage of 0.4. However, the desorption rate constants were much higher on Rh and Ru surfaces as compared to Pt surface. In case of Pt and Ru surfaces this can be easily understood because the exponential term will be much higher on Ru surface compared to Pt due to lower value of $E_{des}$ on Ru relative to Pt and this will result in higher desorption rate constants on Ru. However, the result that Rh has higher values of $E_{des}$ and $k_d$ both as compared to Pt suggests that the pre-exponential factors must be significantly different on these two surfaces. The pre-exponential factors on Pt surfaces must be much smaller as compared to those on Rh surfaces. Similarly this factor on Ru surfaces also must be smaller than those on Rh surfaces for the desorption rate constants to be comparable on these the Rh and Ru catalysts.
3.3. Implications for catalysis

It was observed in this work that there are inherent differences in the mobility behavior of hydrogen on various transition metal surfaces such as silica supported Pt, Rh and Ru. This could be related to the differences in the catalytic activity of these metal catalysts for various reactions. It is known that Rh, Ru and Ir show higher activity for hydrogenolysis whereas Pt is more active for skeletal isomerization (22, 23, 24). Goddard et al. (25) using a kinetic model for ethane hydrogenolysis over Pt, Pd, Ir and Co concluded that the reaction mechanism was significantly influenced by hydrogen partial pressure but not by ethane partial pressure. It has been observed experimentally that the rate of hydrogenolysis of ethane was inversely proportional to hydrogen pressure (3, 22, 23). Many workers (22, 23, 26, 27, 28) have observed that the rate determining step for the ethane hydrogenolysis reaction was the breaking of carbon-carbon bond of dehydrogenated hydrocarbon species, on several transition metals such as Ru, Pt, Rh, Ir etc. Oliver and Kemball (24) found this to be true for Pt and Rh both supported on silica, below 450 K but they observed that desorption of methane became the rate controlling step above this temperature. Frennet et al. (28) observed that desorption of methane was the only irreversible step for ethane hydrogenolysis on an Rh film. The rates for both these steps are dependent on the concentration of adsorbed hydrogen species on the surface. The mobility of hydrogen involving adsorption and desorption, dictates the
concentration of hydrogen on the surface. Hence understanding the kinetics of hydrogen chemisorption is useful in understanding the mechanisms of reactions involving hydrogen.

4. Conclusions

The mobility of hydrogen was higher on Rh and Ru surfaces as compared to that on Pt surfaces. The rate constants for desorption and adsorption of hydrogen as well as the sticking coefficient of hydrogen on Ru and Rh catalysts were found to be higher than that on Pt catalyst. The sticking coefficients of hydrogen decreased in the order of Rh>Ru>Pt. The sticking coefficients on supported metal catalysts were higher than the corresponding single crystal surfaces which suggested that the defect-like sites are highly active for dissociative hydrogen adsorption on these metal surfaces. The desorption rate constants on Rh and Ru were comparable to each other but were higher than those on Pt by a factor of 20 to 40. However, the activation energy of hydrogen desorption was found to decrease in the order Rh>Pt>Ru. This implied that the differences in rate constants were not only due to different activation energies but also due to different pre-exponential factors and this factor must be smaller on Pt and Ru catalysts as compared to Rh catalysts.

Thus the various kinetic parameters for hydrogen chemisorption were different on the silica supported Rh, Ru and Pt catalysts. These could be
responsible for different activity exhibited by these transition metals towards various hydrogenation and hydrogenolysis reactions.

5. Acknowledgments

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-7405-ENG-82, and by the National Science Foundation, Engineering Research Equipment Grant CBT-8507418.

6. References


Table 1

Kinetic parameters for hydrogen chemisorption on silica supported Rh, Ru and Pt surfaces at hydrogen coverage of 0.4:

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<tr>
<th></th>
<th>3% Rh/SiO₂</th>
<th>4% Ru/SiO₂</th>
<th>5% Pt/SiO₂</th>
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<td>Disp.(%)</td>
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<td>20</td>
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<td>T(K)</td>
<td>333</td>
<td>296</td>
<td>333</td>
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<td>$k_{ex}$ (s⁻¹)</td>
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<td>$k_d$ (s⁻¹)</td>
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<tr>
<td>S at 350 K</td>
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<td>$E_{des}$ (kJ/mole)</td>
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<td>43</td>
<td>66</td>
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Table 2

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<th>Sticking Coeff.</th>
<th>Ref.</th>
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Figure Captions

Figure 1. Comparison of experimental selective excitation spectra at different temperatures and simulated spectra with fitted exchange parameters for 3% Rh/SiO₂ catalyst.

Figure 2. Arrhenius plots for (a) 3% Rh/SiO₂ catalysts, (b) 4% Ru/SiO₂ and (c) 5% Pt/SiO₂.

Figure 3. Sticking coefficients of hydrogen on supported and single crystal Pt, Rh and Ru surfaces as a function of hydrogen coverage.
Figure 1.
Figure 2.
Figure 3.
CHAPTER 5. A STUDY OF HYDROGEN CHEMISORPTION ON SILICA SUPPORTED Pt, Rh AND Pt-Rh CATALYSTS

A paper to be submitted to Journal of Catalysis

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Abstract

The dynamics of hydrogen on the surfaces of silica supported Pt, Rh and Pt-Rh catalysts was studied by means of \textsuperscript{1}H NMR selective excitation experiments. The adsorption and desorption rate constants as well as the apparent sticking coefficients of hydrogen on platinum surfaces were observed to be lower than that on rhodium and bimetallic surfaces. The behavior of the Pt-Rh bimetallic catalysts regarding hydrogen mobility was similar to Rh catalysts and this could be due to the structure sensitivity of hydrogen chemisorption. Surface compositions of these bimetallic catalysts were also determined from \textsuperscript{1}H NMR Knight shifts. It was found that the surface was slightly enriched in rhodium in the presence of hydrogen. A comparison of the experimental data
with the atomistic simulations suggested that the heat of adsorption of hydrogen on rhodium is about 10 to 15 kJ/mole higher than that on platinum. The activation energy for hydrogen desorption was found to be about 80 kJ/mole on Rh and Pt-Rh catalysts and about 66 kJ/mole on Pt catalyst from selective excitation experiments.

**Introduction**

Transition metal catalysts such as Rh and Pt are used for many industrially important reactions involving hydrogen such as hydrogenation of olefins and benzene, reduction of ketones and CO hydrogenation (1-4). Hydrogen is an important reactant in alkane hydrogenolysis reactions which are useful for fundamental catalytic studies. Many large scale industrial reactions such as Fischer Tropsch synthesis and steam reforming of naphtha involve reaction of hydrogen with CO or hydrocarbons over transition metal catalysts (1). Hydrogen, adsorbed in various forms, is known to be highly mobile even at room temperature on the surfaces of transition metal catalysts (5,6). The availability and hence the mobility of hydrogen on the surfaces of transition metal catalysts may be important in understanding the mechanisms of such reactions. For example, the increased chain growth probability for Fischer–Tropsch synthesis on Ru catalysts in the presence of alkali metals can be explained in terms of reduction in hydrogen mobility when alkali are present on the surface (7, 8).
The interaction of hydrogen on single crystal Pt and Rh surfaces has been studied extensively in terms of hydrogen binding energies and kinetics of hydrogen chemisorption. The initial sticking coefficient of hydrogen has been reported to be in the range of 0.55 to 0.65 on Rh(111) surface (9, 10). However, Ehsasi and Christmann (11) have reported much higher initial sticking coefficient of hydrogen about 1.0 on Rh(110) and have assigned this higher value to efficient trapping and subsequent dissociation of hydrogen molecules by surface defects present on the crystallographically more “open” Rh(110) surface. The initial sticking coefficients on Pt(111) surfaces have been reported to be much lower in the range of 0.01-0.06 (9, 12). Lu and Rye (12) have reported that the initial sticking probabilities of hydrogen decreases in the order Pt(110) > Pt(211) > Pt(100) > Pt(111) and that the hydrogen adsorption kinetics are proportional to \((1 - \theta^2)\). Several workers (13-16) have reported the sticking probabilities of hydrogen on polycrystalline Pt filaments. Norton and Richards (13) have calculated the rates of hydrogen desorption from Pt filaments and have reported that the sticking coefficient decreases with increasing temperature. There are a few studies (17-20) of hydrogen adsorption on supported Pt and Rh catalysts but those are mainly concerning the nature of adsorbed hydrogen and no study regarding kinetics of hydrogen chemisorption has been done on supported metal catalysts to the best of our knowledge.
It has been observed that Rh has much higher activity for ethane hydrogenolysis as compared to Pt whereas Pt is more active for skeletal isomerization (21, 22, 23). It has been also reported that the rate of hydrogenolysis of ethane decreases with increasing hydrogen pressure (3, 21-24). The rate determining step for this reaction on several transition metals such as Ru, Pt, Rh and Ir, has been reported to be either the breaking of carbon-carbon bond of dehydrogenated hydrocarbon species or the desorption of methane (21, 22, 25-27). The rates for both these steps are dependent on the concentration of adsorbed hydrogen species on the surface which is determined by the hydrogen mobility on the surface. Hence understanding hydrogen mobility in terms of the rates of adsorption and desorption on these surfaces would be relevant to understanding the mechanisms of the model reactions such as ethane hydrogenolysis.

The knowledge of surface compositions is also essential in order to characterize a bimetallic catalyst. The surface compositions are usually influenced by adsorbates under reaction conditions (28-32). Further, the activity per metal site can only be determined for a bimetallic catalyst if its surface composition is known. This is useful in understanding the presence of geometric or electronic effects which can in turn, elucidate the mechanisms of model catalytic reactions.
In this work, the dynamics of hydrogen on the surfaces of Pt, Rh and Pt-Rh bimetallic catalysts supported on silica was studied using $^1$H NMR selective excitation experiments. Using a multisite exchange model of Engelke et al.\cite{Engelke}, values of the activation energy for interparticle motion, the rate constants of hydrogen desorption and adsorption as well as sticking coefficients of hydrogen on Pt and Rh surfaces were obtained. The surface compositions of the bimetallic catalysts were also determined by a method introduced earlier \cite{32,33}.

**Methods**

*Catalyst Preparation*

Platinum and rhodium catalysts supported on silica were prepared by incipient wetness impregnation method using Pt(NH$_3$)$_4$(NO$_3$)$_2$ (AESAR) and Rh(NO$_3$)$_3$$\times$$2$H$_2$O (AESAR) as precursors. Appropriate amounts of the metal salts were dissolved in deionized water and a measured amount of support was added to the solution. The resulting slurry was dried at room temperature for 20 hours and then at 393 K for 8 hours. The Pt–Rh bimetallic catalysts were prepared by co-impregnation method using the same procedure.

All of the catalysts were reduced in flowing hydrogen at 673 K and subsequently washed with hot deionized water to remove residual water soluble impurities and reduced again in the NMR probe. Selective hydrogen chemisorption was used to measure the dispersion of monometallic as well as
bimetallic catalysts according to a method developed by Uner et. al. (34) and these dispersions are listed in Table 1.

The atomistic simulations were done for the bimetallic catalysts according to a method described elsewhere (32). The quantity $\Delta$ used in the simulations corresponds to the difference between the heats of adsorption of $H_2$ on Pt and Rh and is defined as,

$$\Delta = | \Delta H_{ads, Rh} | - | \Delta H_{ads, Pt} | \ldots [1]$$

Since the reported values of heats of adsorption of hydrogen on Pt and Rh vary over a wide range (35, 36), the simulations were done for $\Delta$ values which gave best fit to the experimental results.

**NMR Experiments**

The NMR experiments were carried out using a home built spectrometer with a proton resonance frequency of 250 MHz. The measurements were done using a home-built *in situ* NMR probe connected to a vacuum/dosing manifold which allowed for an easy control of hydrogen pressure during the measurements. All spectra were recorded at a temperature of 304 ± 1K. A dwell time of 5 $\mu$s was used and number of scans varied from 3600 to 7200 with a repetition time of 0.5 s for the NMR spectra. Selective excitation experiments were done using a DANTE pulse sequence consisting of 30 short pulses (5). A pulse separation of 10 $\mu$s was chosen resulting in total duration of 300 $\mu$s for the
DANTE sequence and a hole width of 3.3 kHz. After a recovery period of 10 μs, a final 90° pulse was applied followed by the detection of the free induction decay.

**Results**

The $^1$H NMR spectra for silica supported Pt, Rh and Pt-Rh catalysts at 7 Torr H$_2$ are given in Fig. 1. The surface compositions of the Pt-Rh bimetallic catalysts were determined using Knight shifts from these spectra by a method developed earlier (32) and are plotted in Fig. 2 along with the results of atomistic simulations. The simulations were done for a 31% dispersed particle and a value of 15 kJ/mole for the difference $\Delta$ between the heats of adsorption of hydrogen on Pt and Rh at 673 K as well as for an adsorbate free Pt-Rh surface at the same temperature. The Knight shifts, the dispersions as well as the overall and calculated surface compositions for all the catalysts are given in Table 1.

The simulated pictures for the cubo-octahedron shaped Pt-Rh particle with 50% Pt-50% Rh and dispersion of 31% at 673 K for adsorbate-free and hydrogen covered surfaces are given in Figs. 3 and 4 respectively. It can be noted that much more rhodium is present on the surface in the presence of hydrogen as compared to the adsorbate-free surface. It can be also seen that the edge and corner sites are mainly occupied by platinum on an adsorbate free Pt-
Rh surface whereas those sites are occupied by rhodium on a hydrogen covered Pt-Rh surface.

At a hydrogen coverage of 0.4, the hydrogen-on-metal resonance line was inhomogeneously broadened and selective inversion of population could be achieved. The experimental selective excitation spectra thus obtained were compared with the with the simulated spectra based on the multi-site exchange model developed by Engelke et al. (4). The desorption and adsorption rate constants as well as the apparent sticking coefficients of hydrogen, listed in Table 2, were determined from the exchange parameter according a method described elsewhere (37). The desorption rate constants were 20 to 40 times higher on Rh and Pt-Rh catalysts as compared to Pt catalyst. The adsorption rate constant and the apparent sticking coefficient were also higher on Rh and Pt-Rh catalysts than those on Pt catalyst. The selective excitation experiments were carried out at different temperatures but constant hydrogen coverage and the desorption rate constant $k_d$ was obtained as a function of temperature, from such comparison of experimental and simulated spectra. An Arrhenius plot of the desorption rate constant versus inverse temperature was obtained from this data for Rh/SiO$_2$ as well as for one Pt-Rh/SiO$_2$ and Pt/SiO$_2$ catalyst (see Fig. 5). The activation energy of hydrogen desorption, $E_{des}$, was obtained from such a plot and was about 80 kJ/mole on Rh and Pt-Rh catalysts and about 66 kJ/mole on Pt catalyst at hydrogen coverage of 0.4.
Discussion

Surface compositions

It can be noted that only one upfield peak is seen (Fig. 1) in the spectra for all catalysts that were exposed to 7 Torr of H₂. Further, the hydrogen-on-metal peak shifts toward upfield direction as the overall composition of the catalysts was increased from pure Pt to pure Rh. These observations suggested that the NMR shifts can be used to determine the surface composition of the Pt-Rh bimetallic catalysts. In an earlier work (32), two possible limiting cases of a localized and non-local electronic structure for Pt-Rh bimetals were discussed. According to the localized case, hydrogen is in fast exchange relative to the NMR time scale, between Pt and Rh adsorption sites whereas in the non-local case, the dynamics of hydrogen is not important. In either case, the surface composition of the bimetallic catalysts can be related to the observed $^1$H NMR Knight shifts by the following weighted average expression (32):

$$\delta_{\text{Pt-Rh}} = \delta_{\text{Pt}} X^\text{Pt} + \delta_{\text{Rh}} X^\text{Rh}$$  \[2\]

where $\delta_{\text{Pt-Rh}}$ is the observed shift for hydrogen on a bimetallic catalyst, $\delta_{\text{Pt}}$ and $\delta_{\text{Rh}}$ are the observed lineshifts on monometallic platinum and rhodium catalysts, and $X^\text{Pt}$ and $X^\text{Rh} = 1 - X^\text{Pt}$, are the surface compositions of platinum and rhodium, respectively.

The experimentally determined values of surface compositions (expressed as surface atom fraction of rhodium) are compared in Fig. 2, along with the
values obtained from atomistic simulations involving coordination dependent bond energies. The diagonal line corresponds to no surface segregation and the corresponding value for the difference $\Delta$ obtained from site energies is 9.7 kJ/mole. It was found that the parameter $\Delta$ is insensitive to temperature and the simulations in Fig. 2 were done for a $\Delta$ value of 15 kJ/mole at 673 K. The experimental values lie between this simulated curve and the diagonal line suggesting that the difference $\Delta$ has a value of in the range of 9.7 to 15 kJ/mole. Schoeb et al. (38) performed the atomistic simulations of adsorbate-free surfaces of Pt–Rh bimetallic particles. and observed that platinum segregates to the surface in the absence of any adsorbate. In this work, the experimentally determined values of surface composition suggest that the surface of Pt-Rh catalysts is slightly enriched in Rh but there is no large segregation of any component to the surface in the presence of hydrogen. However, the fraction of rhodium present at the surface is much more under hydrogen atmosphere than the rhodium fraction present at the surface in the absence of hydrogen. These results are similar to those observed on alumina supported Pt-Rh catalysts earlier (32). These results are also in agreement with the results obtained by van Delft et. al. (28, 29) on Pt-Rh single crystal surfaces who reported that hydrogen did not significantly influence the surface compositions of Pt-Rh bimetallic catalysts. Oliver and Kemball (10) did not determine the surface compositions of their Pt-Rh catalysts, but assumed that it was not much
different from overall catalyst compositions. This seems to be valid based on the results presented here, at least when a large fraction of the surface is covered with hydrogen which is true for many hydrogenolysis reactions.

*Dynamics of hydrogen*

The differences in hydrogen mobility on the surfaces of Pt, Rh and Pt-Rh catalysts could be due to influence of surface features of metallic particles on hydrogen chemisorption as discussed below. From the atomistic simulations it can be seen that when hydrogen is not present on the surface of a 50% Pt-50% Rh particle (D=31%), a large fraction of the edge and corner sites is occupied by platinum (Fig. 3). However when hydrogen is adsorbed on the surface of the same Pt-Rh particle, (coverage of $H_2 = 1$, $\Delta = 15$ kJ/mole) most of the edges and corners are occupied by rhodium (Fig. 4). Bernasek and Somorjai (39) observed that the step sites were highly active the dissociative hydrogen (deuterium) adsorption on Pt surfaces. Since these defect-like sites are mostly occupied by rhodium on the Pt-Rh bimetallic catalysts under hydrogen atmosphere, the hydrogen mobility would be similar to pure Rh catalyst. Further the bimetallic surface is enriched in Rh in the presence of hydrogen as compared to the adsorbate-free Pt-Rh surface and this might result in Rh-like behavior of the Pt-Rh catalysts.
The desorption rate constants were higher on Rh and Pt-Rh catalysts as compared to Pt catalyst. For non-activated adsorption such as hydrogen adsorption on transition metal surfaces, the activation energy for desorption would be the same as the heat of adsorption if the process is simple (e.g., Langmuir-like) and there is a single adsorption energy. The activation energy of hydrogen desorption was found to be about 14 kJ/mole higher on Rh and Pt-Rh catalysts (80 kJ/mole) than that on Pt (66 kJ/mole). This difference agrees very well with the range of 10 to 15 kJ/mole obtained for the difference between the heats of adsorption of hydrogen on Rh and Pt from the results on surface compositions.

The sticking coefficients on Pt-Rh bimetallic catalyst with 65 atomic % Rh were similar to those on Rh catalyst because the edge and corner sites are enriched in Rh under hydrogen atmosphere and these sites are highly active for dissociative hydrogen adsorption. Since the sticking coefficient of hydrogen on Pt appears to be quite small at a coverage of 0.4, its value on Pt-Rh catalysts would be mainly governed by the sticking coefficient on Rh. It was shown (4) that interparticle hydrogen motion on Ru/SiO₂ catalysts occurs mainly via the gas phase which means it involves the processes of (associative) desorption from one particle, diffusion in the gas phase and (dissociative) adsorption on another particle. If the processes of hydrogen adsorption and desorption on Pt surface are intrinsically slower than those on Rh surface, then lower hydrogen mobility
on a Pt surface relative to Rh surface can be expected. In case of bimetallic 
catalysts, hydrogen can easily move from Rh atom to Pt atom and back to an Rh 
atom resulting in mobility behavior similar to Rh catalysts.

Conclusions

The surface compositions of silica supported Pt-Rh catalysts were 
determined using the Knight shifts of $^1$H NMR and the surfaces of the bimetallic 
catalysts were found to be slightly enriched in Rh under hydrogen atmosphere 
and significantly different from the surface compositions of the adsorbate-free 
catalysts. A comparison of experimental data with atomistic simulations 
suggested that the heat of adsorption of hydrogen on rhodium was about 10 to 15 
kJ/mole higher than that on platinum. The mobility of hydrogen was higher on 
Rh and Pt-Rh surfaces as compared to that on Pt surfaces. The rate constants 
for desorption and adsorption of hydrogen as well as the sticking coefficient of 
hydrogen on Pt-Rh and Rh catalysts were found to be higher than that on Pt 
catalyst. The processes of adsorption and desorption of hydrogen appear to be 
intrinsically slower on Pt as compared to Rh catalyst. The behavior of Pt-Rh 
catalysts is similar to Rh catalyst because the defect-like sites, highly active for 
dissociative hydrogen adsorption, are mainly occupied by Rh on the bimetallic 
catalysts under hydrogen atmosphere.

Such characterization of bimetallic catalysts in terms of their surface 
compositions under the influence of hydrogen and the mobility of hydrogen on
these surfaces could be useful in understanding the mechanisms of model reactions such as ethane hydrogenolysis as well as industrially important hydrogenation reactions.

Acknowledgments

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References


Table 1

$^1$H NMR results of hydrogen chemisorbed on SiO$_2$ supported catalysts:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Knight Shifts (ppm)</th>
<th>Disp.</th>
<th>Overall Fraction</th>
<th>Surface Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pt</td>
<td>-25</td>
<td>34</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3% Pt - 1% Rh</td>
<td>-102</td>
<td>32</td>
<td>0.39</td>
<td>0.56</td>
</tr>
<tr>
<td>2.6% Pt - 1.4% Rh</td>
<td>-115</td>
<td>56</td>
<td>0.51</td>
<td>0.65</td>
</tr>
<tr>
<td>2% Pt - 2% Rh</td>
<td>-125</td>
<td>45</td>
<td>0.65</td>
<td>0.73</td>
</tr>
<tr>
<td>1.5% Pt - 2.5% Rh</td>
<td>-134</td>
<td>80</td>
<td>0.76</td>
<td>0.79</td>
</tr>
<tr>
<td>1% Pt - 3% Rh</td>
<td>-145</td>
<td>48</td>
<td>0.85</td>
<td>0.87</td>
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<tr>
<td>3% Rh</td>
<td>-163</td>
<td>60</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 2

Kinetic parameters for hydrogen chemisorption:

<table>
<thead>
<tr>
<th></th>
<th>3% Rh/SiO₂</th>
<th>2% Pt - 2% Rh/SiO₂</th>
<th>5% Pt/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ex}(s^{-1})$</td>
<td>2.0x10³</td>
<td>1.0x10³</td>
<td>8.0x10⁰</td>
</tr>
<tr>
<td>$k_d (s^{-1})$</td>
<td>5.0x10³</td>
<td>2.5x10³</td>
<td>2.0x10¹</td>
</tr>
<tr>
<td>$k_a (Pa^{-1} s^{-1})$</td>
<td>3.37x10⁵</td>
<td>1.68x10⁵</td>
<td>1346</td>
</tr>
<tr>
<td>S at 350 K</td>
<td>4.3x10⁻¹</td>
<td>1.6x10⁻¹</td>
<td>8.6x10⁻³</td>
</tr>
<tr>
<td>$E_a$ (kJ/mole)</td>
<td>79</td>
<td>80</td>
<td>66</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. $^1$H NMR spectra for monometallic Pt and Rh and five bimetallic Pt-Rh catalysts supported on silica with 7.0 Torr of hydrogen. The overall mole fraction of rhodium – $X_{\text{Rh}}$ is indicated for each catalyst.

Figure 2. Surface mole fraction of Rh against overall mole fraction of Rh for atomistic simulations at 673 K and experimental data. The values given in the legend correspond to the difference $\Delta$ (defined in the text) between the heats of adsorption of hydrogen on platinum and rhodium in kJ/mole.

Figure 3. Atomistic simulation for an adsorbate-free 50%Pt–50% Rh particle with dispersion of 31% at 673 K. Light atoms are Pt and dark atoms are Rh.

Figure 4. Atomistic simulation for a hydrogen covered (coverage = 1.0) 50%Pt–50% Rh particle with dispersion of 31% and for a $\Delta$ value of 15 kJ/mole at 673 K. Light atoms are Pt and dark atoms are Rh.

Figure 5. Arrhenius plots for (a) 3% Rh/SiO$_2$ catalysts, (b) 2% Pt - 2% Rh/SiO$_2$ and (c) 5% Pt/SiO$_2$ at hydrogen coverage of 0.4.
Figure 1.
Figure 2.

Surface atomic fraction of Rh, $X_{\text{Rh}}^s$

Overall atomic fraction of Rh, $X_{\text{Rh}}^o$

- $\Delta = 15 \text{ kJ/mole}$
- $\Delta = 0 \text{ kJ/mole}$
- $^1\text{H NMR}$
50% Rh 50% Pt
No adsorbate, 673 K

Figure 3.
50% Rh  50% Pt
Hydrogen coverage = 1.0, 673 K

Figure 4.
Figure 5.
CHAPTER 6. STRUCTURE SENSITIVE HYDROGEN ADSORPTION:
EFFECT OF Ag ON Ru/SiO₂ CATALYSTS

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Abstract

The dynamics and energetics of hydrogen chemisorption on silica supported ruthenium and ruthenium-silver bimetallic catalysts were studied by ¹H NMR spectroscopy and microcalorimetry. It was observed that the amount of hydrogen adsorbed on Ru particles decreased with increasing amounts of silver. The populations of hydrogen adsorption states having intermediate and low heats of adsorption were significantly reduced with increasing amounts of silver. The desorption and adsorption rate constants, determined from selective excitation NMR experiments, were lower on Ru-Ag catalyst than those on Ru catalyst at the same temperature and hydrogen coverage. The apparent sticking coefficients of hydrogen on Ru-Ag catalyst with 10 atomic % Ag were 10 times lower than those on Ru catalyst and were comparable to sticking coefficients reported in the literature for hydrogen adsorbing on Ru single crystal. Thus
silver was found to greatly affect both the dynamics and energetics of hydrogen chemisorption on Ru/SiO₂. However, ensemble and electronic effects did not play any role in causing these effects. It is postulated here that the influence of silver was due to its tendency to selectively segregate to edge, corner and other low coordination structures on the Ru particle surface. Hence, hydrogen adsorption on these surfaces was found to be structure sensitive.

1. Introduction

The addition of a second metal to a transition metal can result in marked changes in the surface properties of a catalyst affecting its activity and selectivity for various reactions (1-4). In some cases it is desirable to add a less active metal such as Ag, Au or Cu in order to improve selectivity towards a desired product. For example, Ag was found to increase the selectivity and rate of formation of propionaldehyde during ethylene hydroformylation on Rh/SiO₂ (5). Silver was also found to increase the selectivity towards acetaldehyde on Rh/SiO₂ for CO hydrogenation by decreasing the rates of formation of methane and C₂+ hydrocarbons on these catalysts (5,6).

The Ru-Ag bimetallic system represents a model catalytic system of the type mentioned above. It is well known that noble metals such as Ag and Au do not dissociatively adsorb molecular hydrogen but can adsorb only atomic hydrogen at temperatures below about 195 K (7). Therefore, hydrogen does not
spill over from Ru to Ag or Au at room temperature or higher (8) unlike the Ru-
Cu/SiO₂ system (9). In the absence of such metal-to-metal spillover, the
characterization of the Ru-Ag system is easier because the amount of
chemisorbed hydrogen determined from a standard volumetric method or by
NMR directly relates to ruthenium metal. Further, silver blocks sites on Ru
surface and the effect of Ag blocking sites on the Ru surface can be studied
without the complication of metal-to-metal spillover of hydrogen.

Even though Ag is catalytically inert for many hydrocarbon reactions, it
appears to modify the catalytic activity of Ru/SiO₂. For example, Smale and
King (10) observed that the ethane hydrogenolysis activity (per ruthenium site)
of Ru-Ag/SiO₂ catalysts was much lower than that of Ru/SiO₂ catalysts. They
also observed that the order of the reaction with respect to hydrogen was more
negative on Ru-Ag catalysts as compared to Ru catalysts. The modification of
catalytic activity is usually explained by invoking electronic and ensemble
effects. Electronic effects refer to perturbations in the electronic properties of
the two metals when they are brought into intimate contact. However,
Rodriguez (11) observed using temperature programmed desorption (TPD), X-ray
photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy
(XAES) that an Ag monolayer on Ru (0001) did not cause large electronic
perturbations in the Ru surface.
Ensemble effects usually refer to reduction in the number of active metal sites (composed of ensembles of active atoms) upon addition of second inactive metal. Breaking of Ru ensembles is unlikely in the case of the Ru-Ag system due to the lack of micromixing of these two metals. Atomistic simulations of the Ru-Ag system by Strohl and King (12) indicated that Ag preferentially occupied edge, corner and other low coordination sites. At higher silver contents, two and three dimensional Ag islands on Ru are formed. This view is supported by the experimental results of Schick et al. (13) who observed via photoemission of adsorbed xenon (PAX) and angle resolved ultraviolet photoemission spectroscopy (ARUPS), that Ag preferentially occupied all the step sites when deposited on a stepped Ru surface. The PAX results showed that Ag did form three dimensional islands on flat Ru(0001) surface but not on the stepped Ru surface. The ARUPS results indicated that Ag formed one dimensional rows (trough like structures) on a stepped Ru. Hence both theory and experiment agree that reduction of Ru ensembles by the presence of Ag is not likely to occur. If both electronic and ensemble effects are discounted as potential explanations, other effects must be considered.

The objective of this work was to investigate the effects of silver addition on the hydrogen chemisorption behavior and mobility of hydrogen on Ru/SiO₂ catalysts by means of ²H NMR and microcalorimetry. NMR is a quantitative technique and selective excitation ²H NMR is useful in studying hydrogen
dynamics (adsorption, desorption and surface mobility) relevant in understanding mechanisms of various hydrogenation and hydrogenolysis reactions. Hence NMR was used to determine accurate hydrogen-on-metal isotherms and the kinetic parameters of adsorption and desorption.

Microcalorimetry was employed in this work to give complementary information regarding the energetics of hydrogen adsorption as a function of hydrogen coverage and Ag content. It was found that electronic and ensemble effects were not responsible for affecting the dynamics and energetics of hydrogen on Ru/SiO₂ by Ag addition. Instead, silver was found to affect the kinetics of hydrogen chemisorption by affecting Ru surface features and hydrogen adsorption on these surfaces was found to be structure sensitive.

2. Methods

2.1. Catalyst preparation

All the supported catalysts used in this study had a Ru loading equal to 4% by weight of the total (Ru+SiO₂) content. A 4% Ru/SiO₂ catalyst was prepared from a 1.5% ruthenium nitrosyl nitrate solution (Strem Chemicals) and silica (Cab-O-Sil HS-5) using the incipient wetness impregnation method. A slurry was prepared by impregnating the silica support with an appropriate amount of solution. This slurry was dried overnight at room temperature and then at 383 K for two hours. The catalysts were subsequently reduced in flowing
hydrogen at 673 K. The Ru-Ag/SiO₂ catalysts were prepared by coimpregnation with addition of AgNO₃ and Ru(NO)(NO₃)₃. Ag contents are reported as atomic % of the total metal (Ru + Ag) content. The corresponding wt % of total wt (Ru, Ag and SiO₂) are given in Table 1. All the catalysts were washed 8 to 10 times with 60 ml of hot water to eliminate Na and Cl contamination.

2.2. ¹H NMR

The NMR experiments employed a home-built spectrometer with a proton resonance frequency of 250 MHz. The measurements were done using a home-built in situ NMR probe connected to a vacuum/dosing manifold which allowed for easy control of hydrogen pressure and temperature independently during the measurements. All the catalysts were reduced at 673 K for 2 hours in the NMR sample tube, replenishing fresh hydrogen gas every 30 minutes. Before recording the NMR spectra, hydrogen was dosed onto the sample and equilibrated for 10 minutes. All spectra were recorded either at a temperature of 304 ± 1 K or 400 ± 1 K with a repetition time of 0.5 s. Selective excitation experiments were done using a delays alternating with nutations for tailored excitation (DANTE) pulse sequence of 30 short pulses. A pulse separation of 20 μs was chosen resulting in a total duration of the DANTE sequence of 600 μs and corresponding spectral excitation width of ≈ 1.67 kHz. The overall flip angle of the DANTE sequence was adjusted by varying the width of the short
pulse while the rf amplitude remained constant. After a recovery period of 20 μs, a final 90° pulse was applied followed by the detection of the free induction decay.

2.3. Microcalorimetry

A home built Tian Calvet differential heat flux microcalorimeter based on the design of Handy et al. (14) was used in this work. The catalyst was loaded in a thin walled pyrex NMR tube (Wilmad Glass Co.) connected to a stainless steel volumetric system with greaseless fittings. Static reduction of the catalyst was carried out in situ with the hydrogen replenished every 30 minutes, followed by evacuation at the reduction temperature for a period of time equal to the total time of reduction. The samples were placed in the calorimeter and the system allowed to equilibrate overnight. All differential heats of adsorption measurements were made at 400 K to ensure that adsorbed hydrogen had sufficient mobility to probe the energetics of the entire sample surface (15). In addition, previous NMR studies indicated that the adsorbed hydrogen was highly mobile on a given particle and through the system under the experimental conditions used (16).
3. Results

3.1. $^1$H NMR

The catalysts examined by $^1$H NMR spectroscopy include one Ru/SiO$_2$ catalyst and four Ru-Ag/SiO$_2$ catalysts with atomic loadings of 3%, 10%, 20% and 30% Ag. The spectra at 7 Torr H$_2$ for these 5 catalysts all contain two peaks (see Fig. 1). The downfield peak at around 3 ppm is due to diamagnetic species, e.g., the hydroxyl groups of the silica support and hydrogen spilled over from Ru particles onto the support (17, 18, 19). The upfield peak corresponds to hydrogen adsorbed on Ru particles and it is indicative of a large shift due to the interaction of the proton spins with the metal conduction electrons (Knight shift). The Knight shifts for the various catalysts at 7 Torr H$_2$ were the same around -70 ppm regardless of the Ag content. The Knight shifts obtained by extrapolating to zero hydrogen pressure, given in Table 1, were also around -68 ± 6 ppm and did not vary significantly with the Ag content of the catalysts.

The ratios of hydrogen to surface ruthenium, H/Rusurface, were determined from the NMR spectra taken at 400 K for all the catalysts and are plotted in Fig. 2. Note that the intensity of the hydrogen-on-metal resonance represents hydrogen on the surface of Ru plus the gas phase hydrogen because they are in fast exchange on the NMR time scale. The H/Rusurface values were obtained after subtracting the contribution from the gas phase hydrogen from the total intensity. The amount of gas phase hydrogen was calculated to be about 30% of
the total signal at 700 Torr. The number of surface ruthenium atoms for each

catalyst was determined assuming that the hydrogen-to-surface ruthenium

stoichiometry was 1:1 for strongly bound hydrogen. Strongly bound hydrogen

was characterized as the hydrogen that could not be desorbed during a 10

minute evacuation period at room temperature. It can be seen from Fig. 2 that

H/Ru_{surface} is reduced with increasing amounts of Ag.

At low hydrogen coverages the NMR line due to H/Ru was found to be

inhomogeneously broadened and selective inversion of part of the hydrogen-on-

metal population could be achieved by applying the DANTE pulse sequence

(16). The exchange parameters for interparticle hydrogen motion were
determined by comparing the observed selective excitation spectra with
simulated spectra based on a multi-site exchange model developed by Engelke et

al.(16). The model assumed that hydrogen adsorption and desorption were

second order (dissociative) processes. The adsorption and desorption rate
constants were estimated from the exchange parameters using this model and
are listed in Table 2. The apparent sticking coefficients of hydrogen refer to the

sticking coefficients based on the entire Ru surface (and not on sites with specific

coordination). These were determined based on the definition of sticking

coefficient and using the desorption and adsorption rate constants (20) and are

plotted in Fig. 3 for the Ru/SiO_2 and Ru-Ag/SiO_2 (with 10 atomic % Ag) catalysts.

Also plotted in Fig. 3 for comparison, are the results of Shimizu et al. (21) for
hydrogen on Ru(0001) surface. The apparent sticking coefficients of hydrogen on
the Ru-Ag/SiO₂ catalyst are similar to the single crystal Ru surface and are 10
times lower than those on the Ru/SiO₂ catalyst.

The exchange parameters were determined at various temperatures and
desorption rate constants were extracted from the exchange. An Arrhenius plot
of the desorption rate constant k_d versus 1/T parameters at a hydrogen coverage
of 0.4 is shown in Fig. 4 for Ru/SiO₂ catalyst and Ru-Ag/SiO₂ catalyst with 10
atomic % Ag. An activation energy of desorption of 52 ± 5 kJ/mole is obtained
from this plot for the Ru-Ag catalyst with 10 atomic % Ag at a hydrogen
coverage of 0.4. A somewhat lower value of 43 ± 5 kJ/mole is obtained for the
activation energy of desorption on Ru catalyst at the hydrogen coverage of 0.4.

3.2. Microcalorimetry

In Figure 5 the differential heat of hydrogen adsorption on a series of
Ru-Ag/SiO₂ catalysts is shown as a function of hydrogen coverage expressed as
H/Ru_surface. It was observed that adding Ag does not affect the initial heat of
adsorption indicating the absence of electronic effects. Ag reduced the amount of
hydrogen with an intermediate and low heat of adsorption. It was noted that for
the catalysts with more than 20 atomic % Ag there is a significant reduction in
the amount of hydrogen adsorbed. Interestingly the catalysts with more than 20
atomic % Ag have a H/Ru_surface of approximately one when saturation is
achieved. The intermediate and weakly bound hydrogen (heat of adsorption ≤ 10 kJ/mole) are diminished the most. Further, it should also be mentioned that the catalysts with more than 20 atomic Ag show similar differential heat curves. This suggests that any Ag added beyond 20 atomic % does not significantly affect the energetics of adsorption.

An adsorption energy distribution was also obtained from the differential heat data as shown in Figure 6. The distribution is obtained by fitting a curve to the differential heat data and counting the number of micromoles of hydrogen adsorbed in a given range of heat of adsorption. The amount of hydrogen adsorbed is normalized with respect to the amount of strongly bound hydrogen obtained by chemisorption. Figure 6 shows that even at the 3 atomic % Ag there is a perceptible reduction in the amount of hydrogen having an intermediate (20 - 60 kJ/mole) and weak heats of adsorption (< 20 kJ/mole). At this level of Ag addition the strongly bound hydrogen is not significantly affected. The catalysts with more than 10 atomic % Ag show similar adsorption energy distributions. While the number of strongly bound sites with a heat of adsorption greater than 80 kJ/mole are not affected there is a significant reduction of the amount of hydrogen adsorbed with a heat of adsorption of less than 80 kJ/mole.
4. Discussion

4.1. Effect of Ag on quantity of chemisorbed hydrogen

The H/Ru\textsubscript{surface} ratio decreased as the silver content of the Ru-Ag catalysts increased (see Fig. 2). Silver does not adsorb hydrogen and it does not accommodate hydrogen that could spill over from adjacent Ru atoms (8), but silver can block Ru adsorption sites. However, for those Ru sites still available for hydrogen adsorption at the surface, the stoichiometry of hydrogen adsorption appears to be reduced. This observation is valid at all coverages and pressures. For example, at 460 Torr H\textsubscript{2} the H/Ru\textsubscript{surface} ratio for the Ru/SiO\textsubscript{2} catalyst was approximately 3.5 whereas the ratios were 2.5 and 1.5 on Ru-Ag catalysts with 10 and 20 atomic % Ag, respectively. Similarly, this ratio was about 1.1 for the Ru/SiO\textsubscript{2} catalyst and about 0.2 for Ru-Ag catalysts with 10 and 20 atomic % Ag at a pressure of 0.4 Torr. It was noted via microcalorimetry that the populations of hydrogen associated with intermediate and low heats of adsorption on Ru/SiO\textsubscript{2} were considerably reduced with increasing Ag content. It appears that the reduced stoichiometry is a result of the loss of these intermediate and low energy adsorption states. The volumetric measurements of hydrogen uptake at higher pressures include hydrogen spilled over from Ru particles to the silica support in addition to hydrogen on Ru particles. The very low energy adsorption states no doubt are in this category. However, \textsuperscript{1}H NMR can distinguish between hydrogen on the metal particles and spilled over hydrogen and the NMR results clearly
demonstrate that the population of hydrogen associated with Ru metal particles is also reduced considerably. Possible reasons for reduction in the amounts of chemisorbed hydrogen with increasing silver content of the Ru-Ag bimetallic catalysts are: (i) Silver blocks those Ru sites on the surface where large amounts of hydrogen can be adsorbed; (ii) There is an ensemble effect that changes the nature of a multiple adsorption site; (iii) There is an electronic interaction between Ru and Ag that affects the binding of hydrogen to Ru atoms; or (iv) Silver affects the kinetics of hydrogen chemisorption on Ru surfaces. These cases are discussed below in detail.

4.2. Site blocking and ensemble effects

Atomistic simulations of the Ru-Ag system give information regarding the microscopic distribution of Ru and Ag on bimetallic catalyst particles. From such simulations (10, 12), it is suggested that Ag preferentially occupies the edge, corner and other low coordination sites of the bimetallic particles and at 30 atomic % Ag, almost all the edge and corner sites are occupied by silver. Experimental results tend to support this view (13). It may be postulated that the edge, corner and other defect-like surface features of Ru can accommodate additional intermediate and low energy adsorption states and that blocking these sites preferentially causes a disproportionate reduction in these states. However, simple site blocking can not explain the magnitude of the reduction in
population of hydrogen adsorbed on Ru surface by Ag. The defect-like sites occupy only 10-20% of the surface sites for a catalyst with dispersion in the range of 20 to 30%. To account for such a large drop in the stoichiometry, each of these edge and corner sites must occupy an additional 12 to 20 hydrogen atoms which seems highly unlikely.

It is also unlikely that ensemble effects are present in the Ru-Ag bimetallic system because this system does not exhibit micromixing. Indeed, Ag and Ru do not form bulk alloys because of the severe energy penalty associated with Ru-Ag bonds.

4.3. Electronic interactions between Ru and Ag

In this study we observed that the $^1$H NMR Knight shifts in the limit of zero coverage of hydrogen on Ru adsorption sites in Ru-Ag catalysts were all (within experimental error) about $-68$ ppm (see Table 1). This value is essentially the same as the shift of $-65$ ppm in the limit of zero hydrogen coverage observed on the Ru catalyst. The Knight shift, a result of hyperfine interactions of the unpaired conduction electrons of Ru metal with the probe nucleus (in our case $^1$H), is a measure of the density of the bonding states at the Fermi level. Thus, a lack of change in the Knight shift with increasing amounts of silver indicates that there are no through-metal electronic interactions between Ag and Ru that affects the density of hydrogen-metal bonding states at
the Fermi level. The microcalorimetry results are another indication of this lack of an electronic effect between Ru and Ag. Heats of adsorption in the low coverage region are expected to vary if electronic interactions between Ru and Ag are operable. It was observed that the initial, low coverage heats of adsorption of hydrogen are similar for the Ru/SiO$_2$ and all the Ru-Ag/SiO$_2$ catalysts. The combination of $^1$H NMR and microcalorimetry indicated that there is no rationale to postulate an electronic effect associated with Ru-Ag bimetallics, at least for hydrogen adsorption. This view is also consistent with the XPS results of Rodriguez (11) who reported that a Ag monolayer did not exhibit any electronic interaction with Ru(0001) based on the similarities of the 3d binding energies for pure Ag and a Ag monolayer bonded to Ru(0001). The XAES results of Rodriguez (11) also support the absence of electronic interactions between Ru and Ag as the Auger MVV transitions for Ag/Ru(0001) are shifted by only 0.1 eV toward lower binding energy with respect to those of bulk atoms in pure Ag.

4.4. Effect of silver on kinetics of hydrogen chemisorption

The NMR exchange parameter $k_{ex}$ for hydrogen mobility at various hydrogen coverages determined via the selective excitation experiments were translated into adsorption/desorption rate constants and sticking coefficients (20). These rate constants, listed in Table 2 for Ru/SiO$_2$ catalyst and Ru-Ag/SiO$_2$
catalyst with 10 atomic % Ag for various hydrogen coverages, indicate that Ag has a large impact on the kinetics of hydrogen chemisorption. Since silver does not dissociatively adsorb hydrogen under the conditions studied here, the adsorption and desorption of hydrogen on Ru-Ag catalysts are occurring only on the Ru atoms. The desorption and adsorption rate constants are lower by a factor of 20 to 100 for the Ru-Ag catalyst compared to the Ru catalyst depending on the hydrogen coverage. Similarly, the sticking coefficients were also lower on the Ru-Ag catalyst as compared to the Ru catalyst (Fig. 3). We propose two possible explanations for the lowering of the adsorption kinetics by Ag: (i) The sites blocked by Ag are the most active for dissociative hydrogen adsorption and (ii) Ag distributed on Ru surface inhibits the translational motion of hydrogen atoms and this results in inefficient “trapping”.

(i) The simulations of Ru-Ag system suggested that Ag occupied the low coordination edge and corner sites and we suggest that these are the sites which are highly active for dissociative adsorption of hydrogen. This suggestion is supported by the experimental studies on single crystal surfaces. Bernasek and Somorjai (22) reported that the stepped Pt (997) and Pt (553) surfaces were 100 times more active for hydrogen-deuterium exchange than the Pt (111) surface because of the higher activity for dissociating hydrogen (deuterium) at the step sites. Smith et al. (23) also proposed that the edge sites are more active for dissociative adsorption of hydrogen on supported platinum and palladium
catalysts. Further, it was noted (see Fig. 3) that the sticking coefficients of hydrogen on Ru-Ag catalyst were similar to those on a defect-free Ru(0001) single crystal. Silver occupies the edge and corner sites and can not dissociatively adsorb hydrogen. Hence hydrogen can not adsorb at those sites on the Ru-Ag bimetallic catalysts. This suggests that the hydrogen sticking coefficients were lowered when the edge and corner sites are not available for hydrogen adsorption. Thus blocking of the edge and corner sites by Ag results in lower rates of hydrogen adsorption on Ru-Ag bimetallic catalysts as compared to Ru catalysts. One could characterize this to be structure-sensitive adsorption.

(ii) Silver may restrict the translational mobility of adsorbing hydrogen molecules on the surface. If components of the translational energy perpendicular to the surface are lost, the mobile species can be “trapped” or in this case, dissociate (24). If silver restricts such mobility of hydrogen atoms then the rates of dissociative adsorption will be lowered. However, this mechanism for reduction in rates of hydrogen adsorption seems unlikely for the same reasons as discussed for the possibility of ensemble effects. The clustering nature of Ag in a Ru environment is too high.

The desorption rate constants were also lower on Ru-Ag catalysts compared to the Ru catalyst. In this study the rate constant for hydrogen adsorption on Ru was found to be insensitive to temperature at a given coverage. That is, the adsorption process was not activated. Consequently, the activation energy for desorption should be the heat of adsorption if the process is simple
(e.g., Langmuir-like) and there is a single adsorption energy. The activation energy for hydrogen desorption on Ru-Ag catalyst was found to be about 52 ± 5 kJ/mole at a hydrogen coverage of 0.4. This value is higher than 43 ± 5 kJ/mole, the observed activation energy for desorption on the Ru catalyst at the same coverage. These values do not match the heats of adsorption at that coverage although it is clear that the integral heat of adsorption is higher on the bimetallic catalysts (see Fig. 6). If the desorption rate constant is expressed simply as:

\[ k_d = k_{d0} \exp \left(\frac{-E_{des}}{RT}\right) \] 

where \( E_{des} \) is the activation energy for desorption and \( k_{d0} \) is the pre-exponential factor, then difference in the values of the desorption rate constants for Ru and Ru-Ag can be attributed to the different activation energies rather than a difference in the pre-exponential terms. The lower desorption rate is a consequence of the higher energy binding states of hydrogen on the bimetallic.

The fact that the activation energies for desorption do not match the heats of adsorption at the coverage studied suggests that the adsorption/desorption process is not simply a Langmuir-like adsorption into a single or even multiple adsorption states. We have already suggested that the adsorption process may proceed primarily via dissociative adsorption at the edges, corners and other similar sites on the Ru surface in a structure-sensitive manner. The term coined for this site specific adsorption is "portal" mediated adsorption (25). It is likely
that this process initially produces weakly bound, highly mobile hydrogen that migrates to unfilled, strong binding sites. Indeed, this "precursor" state is consistent with the lack of coverage-dependence of the apparent sticking coefficient at lower coverages on Ru catalyst noted in Fig. 3 (26). Likewise, the desorption process requires two hydrogen atoms combining to form the desorbing molecule. The two atoms may be both strongly adsorbed (SS), both weakly adsorbed (WW), or a combination of weakly and strongly adsorbed species (WS). The relative rates of the elementary desorption processes should be WW >> WS >> SS based solely on the energy barriers.

When the portals are systematically closed, for example, by allowing Ag to distribute to edges and corners, the elementary adsorption processes are shut down, but the desorption process still can occur to the extent that the populations of surface hydrogen exist. Hence, the qualitative picture that emerges is that the weakly bound states are systematically depopulated due to reduced adsorption coupled with desorption favoring the more weakly bound states. The net result is a surface with less total hydrogen and an adsorption energy distribution more heavily weighted to the higher energy states. The calorimetry results (Fig. 5) and the adsorption isotherms (Fig. 2) found in this study are consistent with this model of the adsorption/desorption processes.

The portal mediated adsorption model outlined above can explain catalytic variations previously observed for some bimetallic systems. For example, Smale and King (10) noted that even though Ag is catalytically inert,
does not adsorb hydrogen and cannot produce an ensemble effect, it can significantly alter the ethane hydrogenolysis reaction on Ru. Ru-Ag catalysts yield a significantly more negative order of reaction with respect to hydrogen on Ru-Ag compared to Ru catalysts, -2.5 versus -1.5. In a simple mechanism the effect is the same as if the heat of adsorption of hydrogen was increased (10). The results presented here confirm that the average heat of adsorption is indeed higher on the Ru-Ag bimetallic.

It is not clear how general the understanding of portal mediated chemisorption processes coupled with surface segregation is in the explanation of bimetallic and structure sensitive reactions. But in cases such as Ru-Ag, where electronic and ensemble effects are unlikely it remains an attractive rationale.

5. Conclusions

The amount of hydrogen adsorbed on Ru particles and hydrogen-to-ruthenium stoichiometry was found to be reduced by the presence of silver in the Ru/SiO₂ system as seen by ¹H NMR. Also, from microcalorimetry, the populations of low and intermediate energy binding states of hydrogen were found to be lower on Ru-Ag catalysts as compared to the Ru catalyst. The rate constants for hydrogen adsorption and desorption, determined from selective excitation ¹H NMR, were 20 to 100 times lower on Ru-Ag/SiO₂ compared to Ru/SiO₂ at a given hydrogen coverage. The apparent sticking coefficients of
hydrogen were at least 10 fold lower on Ru-Ag catalyst (10 atomic % Ag) than those on Ru catalyst at the same temperature and hydrogen coverage. However, the $^1$H NMR Knight shifts as well as the initial heats of hydrogen adsorption were found to be similar on Ru/SiO$_2$ and on all Ru-Ag/SiO$_2$ catalysts.

The influence of silver on the hydrogen chemisorption behavior of Ru/SiO$_2$ was neither due to ensemble effects nor due to electronic interactions between Ru and Ag. Further, the blocking of Ru sites by Ag can not cause the large reductions in the hydrogen-to-ruthenium stoichiometry as observed here. The blocking of edge and corner sites by Ag appears to reduce the rates of dissociative hydrogen adsorption resulting in lower populations of low energy binding states of hydrogen which ultimately reduces the rate of hydrogen desorption on the Ru particles. Such reduction in rates of hydrogen adsorption and desorption was responsible for the reduced hydrogen-to-ruthenium stoichiometry on Ru-Ag catalysts as compared to Ru catalyst.

The ruthenium-silver catalysts studied here represent a case of structure sensitive hydrogen adsorption, i.e., blocking of certain sites by silver affects the hydrogen chemisorption on the Ru particles. The results presented here support the hypothesis that the low coordination (edge and corner) sites are active for hydrogen chemisorption and that blocking of these sites by silver hinders the process significantly. This type of site-specific surface segregation could be useful in tailor-making catalysts for reactions where high selectivity towards
some intermediate product is governed by surface hydrogen populations and 
adsorption-desorption kinetics.

Acknowledgments

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References


Table 1.
Atomic and Weight loadings of Ag in Ru-Ag catalysts and Knight shifts of hydrogen on Ru and Ru-Ag catalysts:

<table>
<thead>
<tr>
<th>Atomic % of Ag (Ru+Ag)</th>
<th>Wt.% of Ag (Ru+Ag+SiO₂)</th>
<th>Knight Shifts (extrapolated to zero pressure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>−65</td>
</tr>
<tr>
<td>3</td>
<td>0.13</td>
<td>−70</td>
</tr>
<tr>
<td>10</td>
<td>0.47</td>
<td>−68</td>
</tr>
<tr>
<td>20</td>
<td>1.06</td>
<td>−69</td>
</tr>
<tr>
<td>30</td>
<td>1.79</td>
<td>−65</td>
</tr>
</tbody>
</table>

Note: All catalysts had a Ru loading of 4 wt.%
Table 2.

(a) Desorption and adsorption rate constants for Ru/SiO₂ catalyst at 296K:

<table>
<thead>
<tr>
<th>H/Ruₘ</th>
<th>0.42</th>
<th>0.63</th>
<th>0.73</th>
<th>0.83</th>
</tr>
</thead>
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<tr>
<td>$k_d$ (s⁻¹)</td>
<td>4.8x10²</td>
<td>7.9x10³</td>
<td>2.1x10⁴</td>
<td>2.4x10⁴</td>
</tr>
<tr>
<td>$k_a$ (s⁻¹ Pa⁻¹)</td>
<td>6.3x10⁵</td>
<td>8.7x10⁵</td>
<td>5.7x10⁵</td>
<td>1.5x10⁵</td>
</tr>
</tbody>
</table>

(b) Desorption and adsorption rate constants for Ru-Ag/SiO₂ catalyst at 296 K (10 atomic % Ag):

<table>
<thead>
<tr>
<th>H/Ruₘ</th>
<th>0.42</th>
<th>0.60</th>
<th>0.76</th>
<th>0.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_d$ (s⁻¹)</td>
<td>1.9x10¹</td>
<td>1.0x10²</td>
<td>3.9x10²</td>
<td>1.2x10³</td>
</tr>
<tr>
<td>$k_a$ (s⁻¹ Pa⁻¹)</td>
<td>2.5x10⁴</td>
<td>8.5x10³</td>
<td>1.5x10⁴</td>
<td>9.6x10³</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. $^1$H NMR spectra for SiO$_2$ supported Ru and Ru-Ag catalysts at 7 Torr H$_2$. The Ru weight loading is 4% on all catalysts and the atomic % of Ag in each catalyst is indicated.

Figure 2. Hydrogen adsorption isotherms at 400 K for Ru/SiO$_2$ and Ru-Ag/SiO$_2$ catalysts with 3, 10 and 20 atomic % Ag.

Figure 3. Apparent sticking coefficient of hydrogen as a function of hydrogen coverage on Ru/SiO$_2$, Ru-Ag/SiO$_2$ and Ru(0001) catalysts (21).

Figure 4. Arrhenius type plot of exchange parameter versus inverse temperature for Ru/SiO$_2$ and Ru-Ag/SiO$_2$ with 10 atomic % Ag.

Figure 5. Heats of adsorption of hydrogen as a function of hydrogen coverage for Ru/SiO$_2$ and Ru-Ag/SiO$_2$ catalysts with 3, 20 and 30 atomic % Ag.

Figure 6. Site distribution plot for Ru/SiO$_2$ and Ru-Ag/SiO$_2$ catalysts with 3 and 30 atomic % Ag.
Figure 1.
Figure 2.
Figure 3.
Figure 4.

- 4% Ru/SiO$_2$
  - $E_{\text{des}} = 43 \text{ kJ/mole}$
  - $H/\text{Ru}_g = 0.4$

- Ru-Ag/SiO$_2$ (10 At.% Ag)
  - $E_{\text{des}} = 52 \text{ kJ/mol}$
  - $H/\text{Ru}_g = 0.4$
Figure 5.
Figure 6.
CHAPTER 7. GENERAL CONCLUSIONS

The surface compositions of alumina and silica supported Pt-Rh catalysts were found to be influenced by chemisorbed hydrogen. The surfaces of the Pt-Rh bimetallic catalysts were enriched in Rh under hydrogen atmosphere as opposed to the adsorbate-free Pt-Rh surfaces which are enriched in Pt. It was also found that Pt-Rh catalysts mainly consisted of bimetallic particles with fairly uniform compositions. Further, the heat of adsorption of hydrogen was found to be about 10 to 15 kJ/mole higher on Rh catalysts as compared to Pt catalysts. This understanding can be generalized to predict qualitatively and quantitatively, the surface segregation behavior of a bimetallic system under reaction conditions.

The mobility of hydrogen on Rh and Pt-Rh catalysts was higher than that on Pt catalyst. The rate constants for adsorption and desorption as well as the apparent sticking coefficients were found to be higher on Rh and Pt-Rh than those on Pt. The activation energy for hydrogen desorption was higher on Rh and Pt-Rh than that on Pt while the pre-exponential factors for the desorption rate constant were also higher on Rh and Pt-Rh catalysts as compared to Pt catalyst. The sticking coefficients of hydrogen were higher on supported metal catalysts as compared to single crystal metal surfaces which suggested that the defect-like sites are active for trapping and dissociative adsorption of hydrogen.
The amount of hydrogen adsorbed on Ru particles and the hydrogen-to-ruthenium stoichiometry decreased with increasing Ag content in the case of silica supported Ru-Ag bimetallic catalysts. It was also observed that the desorption and adsorption rates on Ru-Ag/SiO₂ catalyst were lower than those on Ru/SiO₂ catalyst. The populations of states with low and intermediate binding energies of hydrogen were lower on Ru-Ag catalyst as compared to Ru catalyst. This influence of Ag on the dynamics and energetics of hydrogen on Ru particles was not due to ensemble or electronic effects, but was a result of structure-sensitive hydrogen adsorption. Our results support the hypothesis that the low coordination sites are active for hydrogen chemisorption and blocking of these sites by Ag hinders the process significantly. This type of site specific surface segregation can be useful in tailor-making catalysts for reactions where selectivity towards some intermediate product is governed by the concentration of surface hydrogen and the kinetics of hydrogen adsorption-desorption.
APPENDIX A

THE EFFECT OF POTASSIUM ON THE KINETICS AND THERMODYNAMICS OF HYDROGEN ADSORPTION ON Ru/SiO₂ CATALYSTS

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Abstract

Microcalorimetry and ¹H NMR spectroscopy were used to elucidate the effect of potassium addition on hydrogen chemisorption behavior of Ru/SiO₂ catalysts. Three different states of adsorbed hydrogen with significantly varying heats of adsorption were observed by microcalorimetry. The amount of hydrogen adsorbed on the Ru surface decreased with increasing amounts of K additive, which was observed by both NMR and calorimetry. NMR results suggested that certain weakly bound states of hydrogen on Ru were eliminated with large amount of K on the surface and the amount of hydrogen adsorbed on the metal particles decreased with K addition whereas volumetric hydrogen adsorption results suggested that there was a large reduction in spilled over hydrogen.
species too upon K addition. This indicated that potassium blocked certain sites for hydrogen adsorption on the Ru particles as well as sites for spillover on the silica support. Selective excitation NMR experiments suggested that mobility of hydrogen on Ru surfaces was significantly restricted with large amounts of K on the surface. It was further noted that the initial heats of hydrogen adsorption were more or less the same for unpromoted and K promoted Ru catalysts suggesting that K did not exhibit any electronic interaction with Ru particles.

Introduction

Alkali promoters are used in a number of chemical reactions including ammonia production (1) and Fischer Tropsch synthesis (2). In ammonia synthesis over iron, K promoters increase the rate of reaction (3). On the other hand it is well established that in Fischer Tropsch synthesis K promoters increase the selectivity for alkenes while suppressing the rate of reaction (4, 5). While there is agreement regarding these observations there is still controversy regarding the exact mechanism by which alkali exert their influence (6).

Some of the theories (6) which have been proposed for the role of alkali promoters include blocking of chemisorption sites, changes in the electron density at the surface of the metal, direct chemical interactions between the adsorbate and the promoter, through-space interactions (electrostatic in nature), and alkali induced surface reconstruction. Of these various theories the most frequently
encountered ones are the site blocking and electronic effects due to the alkali. Recently, it has also been proposed that another possible explanation is that alkali promoters alter the mobility of hydrogen (7). In this study $^1\text{H}$ NMR was used to show that adding alkali promoters to Ru/SiO$_2$ not only eliminated a weakly bound state observed for hydrogen adsorption on Ru/SiO$_2$ (8) but also reduced the mobility of hydrogen. This effect of alkali promotion will be discussed in the light of the various theories.

It should be mentioned that that most of the theories proposed to date have been based on observations resulting from fundamental studies on alkali promoted single crystal studies under ultrahigh vacuum (UHV) conditions. In most of these studies it is implicitly assumed that the results can be extrapolated to hold under operating conditions on real supported catalysts. While it is true that surface science studies have contributed immensely to our understanding of the role of alkali promoters such extrapolation of surface science results to supported catalysts operated under actual conditions should be done with caution. This is because for supported catalysts additional factors, like surface heterogeneity, the nature of the support, spillover from the metal to the support etc., can play a significant role. Further, recent studies have shown that the conditions under which the studies are made can also bring extra factors or mechanisms into operation. For example, most of the surface science studies of hydrogen interaction with alkali promoted single crystals use atomic alkali but it has been shown (9,10)
that under operating conditions the alkali are too reactive to be in the metallic state and exist as alkali (M⁺, M = Cs, K, Na etc.) ions in compounds. Compared to the metallic state alkali ions have a much lower tendency to donate electrons.

Uner et al. (11) also found that K exists as KOH species on Ru/SiO₂. Thus, it is these discrepancies between conditions of single crystal studies and actual operation conditions which prompted this work. Hydrogen adsorption on promoted and unpromoted silica supported Ru/SiO₂ has been investigated. The various theories of alkali promotion in catalysis and Fischer-Tropsch synthesis, in particular, have been discussed in the light of observations made in this study.

Here microcalorimetry has been combined with NMR to study how the presence of K promoter influences hydrogen adsorption on Ru/SiO₂ catalyst. The advantage of ¹H NMR is that it is a surface sensitive technique which provides quantitative values for the hydrogen associated with the metal. With the in situ NMR technique hydrogen pressures as high as one atmosphere can be used which allows us to study catalysts under conditions closer to the real operating conditions of high pressure and temperature. Microcalorimetry gives us valuable information regarding heats of adsorption of various states of adsorbed hydrogen and is useful in understanding the energetics of hydrogen adsorption on these catalytic surfaces.

In particular the energetics and mobility of hydrogen on Ru/SiO₂ has been examined. The role of alkali additives in Fischer Tropsch synthesis is elucidated
by comparing the interaction of hydrogen with K/Ru/SiO₂ and unpromoted Ru/SiO₂.

Methods

(a) Catalyst Preparation

All the supported catalysts used in this study have a Ru composition equal to 4% by weight of the total (Ru+SiO₂) content. A 4% Ru/SiO₂ was prepared from a 1.5% ruthenium nitrosyl nitrate solution (Strem Chemicals) using the incipient wetness impregnation method. A slurry was prepared by impregnating silica (Cab-O-Sil) with an appropriate amount of solution. The silica had a BET surface area of 300 m²/g. This slurry was dried overnight at room temperature and then at 110° C for two hours. It was then reduced in flowing hydrogen at 375° C. The K/Ru/SiO₂ catalysts were prepared by coimpregnation of KNO₃ with the ruthenium nitrosyl nitrate solution. The K contents are reported as atomic weight % of the total metal (Ru + K) content. As an example, a Ru-K/SiO₂ with 33% K has $33 = \frac{100 \times K \text{ moles}}{K \text{ moles} + Ru \text{ moles}}$. The Ru/SiO₂ catalysts was washed 8 to 10 times with 60 ml of hot water to eliminate Na and Cl contamination.

(b) Microcalorimetry

A home built Tian Calvet differential heat flux microcalorimeter based on the design of Handy et al. (12) was used in this work. The catalyst was loaded in a thin walled pyrex NMR tube (Wilmad Glass Co.) connected to a stainless steel
volumetric system with greaseless fittings. Static reduction of the catalyst was carried out *in situ* with the hydrogen being replenished every 30 minutes. This was followed by evacuation at the reduction temperature for a period of time equal to the total time of reduction. The samples were placed in the calorimeter and the system allowed to equilibrate overnight. All differential heats of adsorption measurements were made at 130°C to ensure the hydrogen adsorbate has sufficient mobility to probe the energetics of the entire sample surface (13).

(c) $^1$H NMR

The NMR experiments employed a home-built spectrometer with a proton resonance frequency of 250 MHz. The measurements were done using a home-built *in situ* NMR probe connected to a vacuum/dosing manifold which allowed for an easy control of hydrogen pressure during the measurements. All the catalysts were reduced at 673 K for 2 hours in the NMR sample tube, dosing fresh hydrogen every 30 minutes. Before recording the NMR spectra hydrogen was dosed onto the sample and equilibrated for 10 minutes. All spectra were recorded either at a temperature of 304 or 400 ± 1 K with a repetition time of 0.5 s. Selective excitation experiments were done using delays alternating with nutations for tailored excitation (DANTE) pulse sequence of 30 short pulses. A pulse separation of 20 μs was chosen resulting in a total duration of the DANTE sequence of 600 μs and corresponding spectral excitation width of ≈ 1.67 kHz. The overall flip angle of the DANTE sequence was adjusted by varying the width
of the short pulse while the rf amplitude remained constant. After a recovery period of 20 μs, a final 90° pulse was applied followed by the detection of the free induction decay.

**Results**

(a) Microcalorimetry

In this work the differential heats of adsorption have been determined as a function of coverage expressed in terms of H atoms adsorbed per surface Ru metal atom. Note that the amount adsorbed includes hydrogen spillover to the support. The optimized volumetric hydrogen chemisorption technique proposed by Uner et al. (14) was used to determine the metal dispersion. NMR has also been used to determine metal dispersions. The dispersions are tabulated in Table 1. Where ever available the dispersions obtained from NMR have been used in the calculations as NMR is a better measure of the hydrogen associated with the surface Ru than the volumetric technique for the latter technique measures the total hydrogen uptake which includes spillover hydrogen. The increase in dispersion of supported transition metal with the addition of alkali species has been observed before (10, 15, 16).

In Figure 1 the differential heats of hydrogen adsorption on a 4% Ru/SiO₂ catalyst are compared with a series of K promoted catalysts. The promotion levels used were 6, 33 and 50 metal atomic % K. All catalysts, both K promoted and pure Ru, have the same initial heat of adsorption at about 90 kJ/mole. For
all promoted catalysts the results follow the similar trend of a rapid decrease in the heat of hydrogen adsorption with coverage. From Figure 1, it is also observed that adding more than 33 atomic % K eliminates states of intermediate as well as states of low heat of adsorption. Three distinct regions can be identified on this plot. The nature of the hydrogen adsorbed in each of these regions will be considered in the discussion section.

(b) $^1$H NMR

An unpromoted Ru/SiO$_2$ catalyst with 4% loading by weight and two 4% Ru/SiO$_2$ catalysts with 6 and 66 atomic % K were used for the NMR studies. The hydrogen to surface ruthenium ratios (H/Ru$_{surface}$) were determined quantitatively from the NMR spectra taken at 400 K for all the catalysts and are plotted as a function of pressure in Fig. 2 for the above catalysts. Compared to the unpromoted Ru catalyst the H/Ru ratio is less on the catalyst with 6 atomic % K and is even further reduced at the 66% promotion level. It is also observed that with increasing hydrogen pressure the H/Ru ratio increases slightly for the catalyst with 6% K but remains more or less constant for the catalyst with 66% K. The ratios reported in Fig. 2 are obtained after subtracting the contribution from the gas phase hydrogen and the amount of gas phase hydrogen was calculated using the ideal gas law.

All the NMR spectra (Figs.3 and 4) show two peaks at 304 K and 7 Torr. The downfield peak at around 3 ppm is due to diamagnetic species which
correspond to hydroxyl groups of silica support and hydrogen spilled over from Ru particles onto the support. The upfield peak corresponds to hydrogen on Ru surface which exhibits large Knight shifts due to interaction of proton spins with the conduction electrons of the metal.

The selective excitation experiments yield information regarding mobility of hydrogen on the catalyst surface as reported in detail by Engelke et. al.(17). For the 4% Ru/SiO₂ catalyst with 6 at. % K, selective population inversion could not be achieved at 7 Torr H₂ and the NMR line gets saturated instead (see Fig. 3). The line was homogeneously broadened which corresponds to fast interparticle motion of hydrogen on the catalyst surface. On the other hand, selective inversion of a narrow frequency band could be achieved for the H/Ru resonance on the 4% Ru catalyst with 66 at. % K at 7 Torr H₂ and the NMR line was inhomogeneously broadened. (see Fig. 4). This suggested that interparticle motion of hydrogen is restricted on such a catalyst. This implied that the hydrogen on the surface of Ru particles did not exchange with gas phase hydrogen. This is also supported by the constancy of Knight shift on this catalyst with increasing hydrogen pressure. From Figure 5 it is seen that on increasing the hydrogen pressure from 7 to 460 Torr, the Knight shift remained more or less constant around -50 ppm. In fact a narrow gas phase peak superimposed on the silanol peak, can be seen near zero ppm on this catalyst at higher pressures.

This observation, combined with the observation from Figure 2 that the
H/Ru_{surface} ratio does not increase with hydrogen pressure, implies that hydrogen adsorption does not occur after a coverage of about a monolayer. For the catalyst with 6\% K, the Knight shift (for the α peak) changed from -65 to -30 ppm as the hydrogen pressure was increased from 7 to 460 Torr (see Fig. 6). This implied fast exchange between hydrogen on Ru surface with the gas phase hydrogen and this is supported by the results of selective excitation experiments on this catalyst.

The experimental and simulated spectra for Ru catalyst with 6 \% K at various temperatures are shown in Fig. 7. The simulations were done on the basis of a multi-site exchange model developed by Engelke et. al.(18). A comparison of experimental spectra with simulations yields the exchange parameter \( k_{ex} \) for the fast intraparticle motion of hydrogen on the surface of an Ru particle at that temperature. The exchange parameter was shown to be equivalent to the rate constant for desorption \( k_d \) by Engelke et al.(18). Based on this, the desorption rate constant can be obtained as a function of temperature which yields the value of activation energy for desorption \( E_{des} \) or heat of adsorption. An Arrhenius type plot of exchange parameter \( k_{ex} \) versus \( 1/T \) gives a value of about 56 kJ/mole for \( E_{des} \) at a hydrogen coverage of 0.4 for the catalyst containing 6\% K (see Fig. 8). This is in agreement with the results of microcalorimetry.
(c) $^1$H NMR and microcalorimetry

In figure 9 the differential heats of adsorption and the H/Surface Ru are plotted as a function of pressure for 4% Ru/SiO$_2$ and 6%K/Ru/SiO$_2$. It is to be noted that the H/Surface Ru ratio obtained by the volumetric method measures the total hydrogen uptake, including spillover, while the H/Surface Ru ratio obtained by NMR is a measure of the hydrogen influenced by Ru metal (on or around the Ru metal). It is observed that at a given pressure, for both the unpromoted and K promoted catalysts, the H/Ru ratios determined by the volumetric technique exceeds that obtained by NMR. Further, adding K reduces the H/Ru ratio obtained by both techniques. The decrease in H/Ru ratio obtained from NMR suggests that for a given pressure adding K reduces the stoichiometry of hydrogen associated with the metal. At a given pressure the decrease in the H/Ru ratio obtained from volumetric chemisorption is much greater than the decrease in the H/Ru ratio measured using NMR. This suggests that adding K also reduces the amount of hydrogen that spills over to the support.

Discussion

The NMR and microcalorimetric results suggest that adding K promoter to Ru/SiO$_2$ influences the amount of hydrogen adsorbed as well as the mobility of hydrogen on the catalysts surface. The following observations are made from Figures 1 and 9. First, three distinct regions are identified on the differential
heat of adsorption plot. It is noted that a small amount of K can reduces the population of intermediate as well as weakly bound states. Above that small amount of additive the amount of adsorbed hydrogen per available surface Ru and the energetics of these populations are not altered by additional K. Second, initial (low coverage) heats of adsorption are unaffected on K addition. Third, for a given pressure the H/Surface Ru is lower in the presence of K promoter compared to the unpromoted Ru/SiO₂. Fourth, the amount of hydrogen which spills over to the support is reduced in the presence of K promoter. Fifth, large amounts of K reduce the mobility of hydrogen on the catalyst surface. The following paragraphs will discuss how these effects may arise and their implication for catalysis. Wherever possible the microcalorimetry and NMR results will be interpreted in the light of each other.

(a) Adsorbed states of hydrogen

In the differential heat of adsorption plot shown in Figure 1 three distinct regions can be identified. The basis for the division is arbitrary but earlier NMR results provide some justification based on the attributes of the hydrogen observed in these regions. Before describing the hydrogen in the three regions what is currently known regarding hydrogen adsorption on Ru/SiO₂ and K/Ru/SiO₂ is briefly discussed. In particular information regarding the various species identified and there characteristics as determined by ¹H NMR and
microcalorimetry will be presented. It should be highlighted that one or more of these species can be present in each of the three regions identified in figure 1.

Bhatia et al. (8) observed two NMR resonance peaks for hydrogen on pure Ru/SiO₂ at pressures greater than 100 Torr. The first resonance, labeled the α peak, is observed at ~ −60 ppm and the second resonance, called the β peak, occurs at ~ −30 ppm. Engelke et al. (17) used 2D NMR to show that under evacuation the α peak consists of a dissociated species, α₁, with restricted mobility and becomes a more mobile species, αₘ, in non-evacuated samples at higher pressures. It was also shown that the αₘ species and the β species were in slow exchange with a time constant on the order of 1 ms. The β species represented weakly bound hydrogen in fast exchange with the gas phase, as revealed by the pressure dependence of its resonance shift. The exact location of the β hydrogen is not known. Engelke et al. (18) have also showed that the transition from the immobile α₁ species, which is characterized by an inhomogeneous NMR lineshape, to the more mobile αₘ species, characterized by a homogeneous NMR line shape, occurs at a hydrogen to Ru coverage of approximately 0.5.

Bhatia et al. (8) observed that the heat of adsorption of the α species was between 70 and 40 kJ/mole and that it existed in the between 10⁻² to 10 Torr. The authors applied the Clausius-Clapeyron equation to the β peak and obtained
an isosteric heat of adsorption of 7 kJ/mole. This corresponds to the value of approximately 10 kJ/mole obtained by microcalorimetry.

Uner et al.(11) used $^1$H NMR to study hydrogen adsorption on K/Ru/SiO$_2$ (11) and Cs-promoted Ru-Na/SiO$_2$ (5). In both these studies the authors found no evidence for a ruthenium mediated electronic interaction between the alkali species and adsorbed hydrogen. It was found that the K promoter distributed itself between the Ru metal and the silica support. The K blocked hydrogen adsorption sites on the metal though not on a one-to-one ratio as observed by other researchers (19). Further, TGA studies were used to show that K probably existed as an oxide and not in the metallic state. The authors also observed that adding K reduced the intensity of the diamagnetic resonance due to the silanol protons. This implied that the in the presence of K the hydrogen spillover to the silica support is reduced.

The $^1$H NMR work done in this study suggest that increasing amounts of K promoter progressively inhibits the mobility of hydrogen on the surface and its exchange with the gas phase hydrogen. At high K concentrations the $\beta$ peak observed on unpromoted Ru/SiO$_2$ is eliminated.

With this background of information regarding hydrogen chemisorption on pure and promoted Ru/SiO$_2$ the nature of the hydrogen in the three regions is discussed next.
Region I. This is the low pressure region where the H/Surface Ru ratio is less than one. Here the hydrogen adsorbs dissociatively as strongly bound atomic H and has the characteristics of the α species identified by NMR. At low coverages the hydrogen is immobile but the mobility increases with coverage. Most of the hydrogen resides on or near the Ru metal.

It is seen that adding small amounts of K does not alter the adsorption characteristics in this region. On the other hand the catalysts with more than 33 atomic % K show identical initial heats of adsorption but the heats of adsorption rapidly decrease to small values at a H to surface Ru ratio of about one. At high concentrations of K not only is the H/Surface Ru reduced but on the basis of the \textsuperscript{1}H NMR hole burning experiments it can be concluded that the presence of large amounts of promoter reduces the mobility of hydrogen on the surface and its exchange with the gas phase.

Region II. This is an intermediate region with 1 < H/Surface Ru < 2.5 and consists of mobile hydrogen of intermediate bond strength. The large difference between the H/Surface Ru ratios determined by the volumetric method and by NMR, observe in Figure 2, suggests that spillover from the metal to the silica support is significant. An irreversibly bound, spilled over hydrogen was also observed by Uner et al. (14) who used \textsuperscript{1}H NMR and volumetric chemisorption to study hydrogen adsorption on Ru/SiO\textsubscript{2}. A stoichiometry of adsorption of greater than one cannot be ruled out in this region.
The presence of even small amounts of K decreases the amount of hydrogen with intermediate heat of adsorption. In the catalysts with more than 33% K the states with intermediate heat of adsorption are eliminated. The NMR results discussed above also support the conclusion that the presence of alkali promoters reduces the amount of hydrogen adsorbed by decreasing the spillover to the silica support. It is conjectured that at high K concentrations the spillover, if at all there is any, is reduced compared to the unpromoted Ru/SiO₂.

Region III. This is the high pressure region with H/Surface Ru greater than 2.5 consisting of weakly bound, mobile atomic hydrogen in fast exchange with the gas phase. It is postulated that the hydrogen in this region can be correlated with the β species identified by NMR. Thus, the hydrogen is also in fast exchange with the gas phase. At the high pressures used in this region there is significant spillover from the metal on to the support.

Adding small amounts of K slightly reduce the heats of adsorption in this region. For K promotion levels greater than 33 atomic % this region is absent.

(b) Initial heats of H₂ adsorption on Ru/SiO₂ and K/Ru/SiO₂

Any alteration of the metal-adsorbate bond strength due to alkali induced electronic or electrostatic effects should be reflected in a modified heat of adsorption. From Figures 1 and 9, it is seen at low coverages the differential heats of H₂ adsorption are similar on the K promoted and unpromoted Ru/SiO₂. The initial heat lies between 85-90 kJ/mole (error is ± 5kJ/mole) compared to the
initial values of 80 kJ/mole (20) and 120 kJ/mole (21) observed for hydrogen adsorption on Ru[0001] single crystals. The similar heats of adsorption suggests that there is no electronic or electrostatic effects on hydrogen adsorption due to K addition. The low coverage region is of interest as complications due to adsorbate-adsorbate interactions are not present here and any electronic or electrostatic field effects should be most pronounced in this part of the differential heat curve. Praliaud et al. (22) observed that heats of hydrogen adsorption decreased on addition of K to Ni/SiO$_2$. It should be mentioned that the authors obtained the heat of adsorption indirectly from kinetic studies assuming that the heat of hydrogen adsorption was not a function of coverage. Dry et al. (23) also observed a decrease in the initial heats of hydrogen adsorption on iron films and iron oxides on adding K$_2$O but the measurements were made at 20°C. Martinez and Dumesic (13) suggest that this temperature is too low to accurately probe the catalyst surface.

Under the conditions used in the present study the interparticle motion is rapid even at room temperature as demonstrated by the NMR selective excitation study. Hence, the observed initial heats of adsorption accurately reflect the energetics of adsorption.

The location of the K on the surface of the catalyst plays an important role in the interpretation of why similar heats are observed on both the promoted and unpromoted catalysts. Thus, available evidence regarding the location is
reviewed before addressing the similarity of initial heats. There is direct
evidence regarding the location of alkali on Ru(0001) surface from Low Energy
Electron Diffraction (LEED) studies done by Gierer et al.(24). They have carried
out systematic studies of alkali metals (Cs, K, Na and Rb) adsorbed on Ru(0001)
with emphasis on local adsorption geometries. They report that adsorption sites
occupied by alkali metals depend on the alkali coverage and size of alkali adatom.
They further observed that potassium occupied the three fold hollow sites on
Ru(0001) surface whereas on-top sites on Al(111), Cu(111) and Ni(111). However,
Wagharay et al.(25) based on evidence from their IR studies on K promoted
Ru/SiO₂ catalysts report that the alkali metals occupy edge and corner sites.
(Certain Ruthenium carbonyl species were not observed in the IR spectrum of K
promoted Ru catalysts and they inferred that the species could not be formed
because the defect like sites were blocked by the K additive). On supported
catalysts, alkali may not be in metallic form but could be present either as an
oxide or hydroxide and could be occupying sites other than the three fold hollow
sites observed on single crystal surfaces.

Chow and Chelikowsky (26) used ab initio pseudopotentials within the
local-density-functional approximation to conclude that for a monolayer coverage
the three fold hollow site is energetically the most favorable for hydrogen
adsorption on Ru[0001]. Atomistic simulations (27) with Ru-Ag bimetallic
systems have shown that at small concentration Ag preferentially occupies the
edges and corner sites, i.e. the defect-like sites on the surface. Further, the hydrogen adsorption characteristics are similar on Ru-Ag/SiO₂ and Ru/K/SiO₂ (28). Thus, it is postulated that K would preferentially occupy the defect-like sites leaving the three-fold hollow sites vacant. Another fact which has to be considered is the relative rates of adsorption and desorption of hydrogen at various catalyst sites. Bernasek and Somorjai (29) have shown that the dynamics of adsorption and desorption of hydrogen is faster at defect-like sites than on the low index planes. Thus, with the defect-like sites preferentially occupied in the presence of K the dynamics of adsorption and desorption is slowed down but this does not affect the number of empty three-fold hollow sites occupied at equilibration. Hence, it is postulated that at low hydrogen coverages or pressures, even in the presence of K, the hydrogen occupies the three-fold hollow sites which are still vacant as the K preferentially occupies the defect-like sites, resulting in similar initial heats of adsorption on the unpromoted and K promoted Ru/SiO₂.

(c) Effect of K addition on amounts and energetics of H₂ chemisorption on Ru metal

An interesting observation made from Figure 1 is that adding even 6 atomic % K causes a significant reduction in the amounts of hydrogen adsorbed. From Figure 9 it is seen that, for a given pressure, the presence of small amounts of K decreases the H/Surface Ru ratios obtained by the volumetric method and NMR. The difference between the ratios obtained by the two methods,
particularly at higher pressures, suggests that not all the hydrogen adsorbed is on the metal but some of it spills over to the support. Here possible reasons for the decrease in the H/Surface Ru ratios obtained by NMR are discussed. The decrease in the spillover amounts will be examined in the next section.

Single crystal studies of hydrogen adsorption on alkali promoted Ni, Mo, Pt, W and Ru (30 and references therein) show an exponential reduction in the initial sticking coefficient and amount of hydrogen adsorbed as K coverage increases. The reduction in the amounts adsorbed in the presence of K is in agreement with the observations made in this work for hydrogen adsorption on silica supported K/Ru/SiO₂. Kiskinova (30) has reviewed the alkali promoted single crystal systems and postulates that the diffusion of the H₂ precursor, in order to lose energy and accommodate with the surface, before dissociation, could play an important role. Consequently, introducing an alkali additive constrains hydrogen surface diffusion and inhibits dissociative hydrogen adsorption. Studies with Li, Na and K promoted Al(100) (31, 32) show that Al(100) preserves its capacity for atomic H adsorption. When molecular hydrogen is introduced, it results in a lower hydrogen coverage for the promoted catalyst as compared to the unpromoted catalyst. However, with atomic the hydrogen coverage is similar in both cases. This suggests that addition of alkali reduces the dissociation channels and/or blocks adsorption sites at least on single crystals promoted with zero valent alkali.
Uner et al. (11) used $^1$H NMR to conclude that the K promoter added to Ru/SiO$_2$ does block sites for hydrogen adsorption on the Ru metal, but not on a one-to-one basis. Hoost and Goodwin (19) reported a one-to-one blocking of adsorption sites with K loading on Ru/SiO$_2$ but the authors had not accounted for spillover while characterizing their catalysts. Since then the volumetric hydrogen chemisorption technique for determining dispersion of Ru/SiO$_2$ has been optimized to account for spillover (14). Another possible explanation for the reduction in the H/Surface Ru based on the kinetics of hydrogen adsorption and desorption is discussed in the following paragraphs.

Studies by Bernasek and Somorjai (29) indicate that at low pressures the hydrogen-deuterium exchange reaction occurs significantly faster on stepped Pt(997) and Pt(553) surfaces than on Pt(111). They attributed this to enhanced activity for dissociating hydrogen (deuterium) at the step sites. Analogously, Smale and King [27] studied hydrogenolysis on Ru-Group Ib catalysts and postulated that Group Ib metal preferentially occupied defect-like sites and, thus, changed the rate of hydrogen adsorption and desorption from the surface. The authors suggested that hydrogen adsorption-desorption occurs predominantly on the defect-like sites and the Group Ib metal preferentially blocking these sites was the reason for the observed variation in catalytic activity as well as the observed kinetic dependence on hydrogen pressure. From Figure 9 it is seen that the H/Surface Ru reduced in the presence of K promoter. Thus, in this work too it
appears that defect-like structures can greatly influence the population of hydrogen and the thermodynamics of adsorption. Similarity of the differential heat of H\textsubscript{2} adsorption on K/Ru/SiO\textsubscript{2} and Ru-Ag/SiO\textsubscript{2} (28) suggests that K either blocks or alters the edges, corners and defect-like sites preferentially. Assuming a Langmurian model for the hydrogen adsorption-desorption equilibrium we have

$$\theta_H = \frac{(K_H P_H)^{1/2}}{1 + (K_H P_H)^{1/2}}$$

If the defect-like sites have a much higher value for the equilibrium constant K and the potassium promoter preferentially occupies the defect-like sites, then too, smaller equilibrium coverages will be got in the presence of the promoter. In other words a higher pressure is needed to produce a given H/Surface Ru ratio in the presence of K promoter compared to the unpromoted catalyst.

(d) Effect of K addition on hydrogen spillover

Uner et al. (14) used \textsuperscript{1}H NMR to show that hydrogen spills over from the metal to the silica support. The authors showed that the silanol proton intensity increased and that the hydrogen is irreversibly bound to the silica. Further, it was found that the amount of spillover was a strong function of the catalyst reduction temperature, hydrogen adsorption temperature, and the exposure times. This accounts for the significantly higher values of H/Surface Ru ratios obtained by the volumetric method compared to the H/Surface Ru values obtained
by $^1$H NMR. From Figure 9 it is seen that adding even small amounts of K reduces the H/Surface Ru ratios obtained by both methods.

The much larger values of $H/Ru_{surf}$ obtained by volumetric method than by $^1$H NMR suggests that significant spillover occurs on Ru/SiO$_2$. The decrease of the H/Surface Ru ratio in the presence of K promoter is partially accounted for by a reduction in the hydrogen residing on the metal. This is implied by the lower H/Surface Ru ratios obtained by $^1$H NMR in the presence of K promoter than on the pure Ru/SiO$_2$. But not all the decrease in the H/Surface Ru ratio got via the volumetric method can be accounted for by the reduction in the hydrogen residing on/or near the Ru metal. This is especially true at higher pressures. For example, at around 80 Torr the H/Surface Ru ratios obtained by the volumetric method decreases from 9, on the pure Ru/SiO$_2$, to 4 on the catalyst with 6 atomic % K. At the same pressure the H/Surface Ru ratios obtained by $^1$H NMR decreases from 2.25 on the pure catalyst to about 1.5 on the promoted catalyst. This suggests that in the presence of K promoter there is a reduction in the amount of hydrogen spilling over to the silica support.

Uner et al. (11) have used $^1$H NMR to show that on adding K promoter to Ru/SiO$_2$ the K partitions itself between the silica support and the Ru metal. In the same work the authors observed that the silanol proton intensity is also reduced in the presence of K. This suggests that on adding K promoter the K reacts with sites in the silica support which, in the unpromoted catalyst, are
occupied by spilled over hydrogen. It is known that on reduction the silica undergoes dehydroxylation. Thus, it is postulated that on adding K promoter to the Ru/SiO₂ the amount of spillover is probably decreased due to a combination of one or more of the following factors. First, it is seen that in the presence even small amounts of K the hydrogen residing on/or near the Ru metal is reduced due to blockage of adsorption sites and/or the kinetics of the adsorption/desorption process being affected. Further, the K promoter probably blocks sites on the silica support which could have otherwise accommodated spilled over hydrogen.

(e) Mobility of hydrogen

From selective excitation experiments, it is seen that adding large amounts of potassium (for example, 66 atomic % K) restricts the mobility of hydrogen. The exchange of hydrogen on Ru surface with the gas phase hydrogen and, hence, the interparticle motion of hydrogen is reduced on this catalyst. It was observed that the hydrogen mobility was lowered on addition of Ag to Ru/SiO₂ catalysts (28) because Ag is known to block defect like edge and corner sites (27). K is also proposed to block these sites on Ru particles in addition to the sites on the silica support for hydrogen spillover from Ru particles (15). Blocking of the defect like edge and corner sites on Ru particles results in reduced rates of hydrogen adsorption and desorption which ultimately results in reduced hydrogen mobility. A gas molecule incident on a solid surface gets trapped on the surface after an inelastic collision. The determining factor for trapping is the loss of its kinetic
energy perpendicular to the surface. If the components of its translational energy parallel to the surface are not lost, a mobile trapped species occurs on the surface [33]. If the channels for such a translation are blocked then the mobility of the species will be quite restricted which was found to occur in this work with large amounts of K added to Ru/SiO₂ catalyst. If the spilled over hydrogen provides alternative paths for translational motion of hydrogen then blocking of such sites would block these paths and this would result in reduced hydrogen mobility upon K addition to the catalyst.

The reduced hydrogen mobility could be the reason for decreased hydrogenation capacity of Ru catalysts for Fischer-Tropsch synthesis upon K addition. Lower mobility of hydrogen would decrease the probability of combination of hydrogen with other reactants such as CO or hydrocarbon fragments. This could result in lower selectivity for alkanes (saturated hydrocarbons) and increased selectivity for alkenes (unsaturated hydrocarbons).

(f) Implications for catalysis

At this point it should be mentioned that the existing theories on the role of alkali promoters in CO hydrogenation have mostly been based on observations with CO or hydrocarbon interaction with alkali rather than on the interactions of hydrogen with alkali (34 and references therein). CO is a polar molecule and it is well established in the literature (35) that any additive or process which increases the electron density at the surface should increase the dissociation rate
of CO (Blyholder's model (36)). On Ru, the dissociation of CO is fast compared to the hydrogenation of surface carbon (37, 38). Thus, even though the K promoter enhances the rate of CO dissociation this process is probably less important than the role of hydrogen in reaction steps like chain growth and termination. From a kinetic standpoint it is more important to focus on the influence of alkali on other processes like hydrogenation, chain propagation and deactivation of surface carbon (39). Thus, it is important to elucidate the role of hydrogen and its interaction with alkali in order to understand the role of alkali promoters in Fischer Tropsch synthesis. In the following discussion the observations made in this study with respect to hydrogen adsorption on K/Ru/SiO₂ are discussed in the light of the different theories of alkali promotion.

As discussed earlier the similarity of the initial (low coverage) heats of hydrogen adsorption on pure Ru/SiO₂ as well as K/Ru/SiO₂ and Ru-Ag/SiO₂ suggest that there is no electronic effect. The same inference was made by Uner et al. (11) who used ¹H NMR to study hydrogen adsorption on K promoted Ru/SiO₂. Further, it should be mentioned that strong electronic interactions of alkali with metal have been suggested in single crystal studies where zero valent alkali was studied (40). However, in catalysts like the ones used in this study the potassium is present in the form of a K⁺ ion in various compounds of potassium (11 and references therein). Compared to its zero valent state, K⁺ is significantly less inclined to donate electrons. The Knight shifts on the Ru catalysts with 6
at.% and 66 at.% K, extrapolated to zero hydrogen pressure are -65 and -47 ppm respectively. Although this difference appears to be large, a similar difference of about 10 ppm was reported by Uner et. al.(11) when the potassium coverage of their Ru catalysts varied from 10 to 90%. This difference has been attributed by Uner et. al. to experimental error.

In the literature it has been proposed that K promoters block the defect like edge and corner sites on Ru particles. Wagharay et. al.(25) proposed this based on their IR study of unpromoted and K promoted Ru/SiO₂ catalysts. These sites are known to be predominantly active for dissociative adsorption /associative adsorption of hydrogen. Hence blocking of these sites by K would reduce the amount of hydrogen adsorbed on Ru surface. There was decrease in amounts of spilled over hydrogen too upon addition of K to the Ru catalyst. This was explained on the basis of blocking of sites available for hydrogen spillover onto the silica support. This also brings about reduction in hydrogen mobility. Thus, site blocking appears to be the dominant mechanism for reduced amounts of hydrogen and reduced hydrogen mobility upon addition of K to Ru/SiO₂ catalysts.

As noted above, the structure of the catalyst and the presence of defect-like sites appears to play an important role in the significant reduction in the amounts of adsorbed hydrogen observed on adding K to Ru/SiO₂. While site blocking and direct chemical interactions between K and adsorbed H cannot be ruled out it appears from the observations in this study that adding K decreases
the amounts of hydrogen adsorbed by influencing the dissociation and mobility of hydrogen on the surface. The $^1$H NMR work done in this work show that at high K concentrations the mobility of hydrogen on the catalyst surface is reduced along with a decrease in the exchange with the gas phase. This observation has an important bearing on the role of hydrogen in various chemical reactions where hydrogenation is important and alkali additives are used. An example of such a reaction is Fischer Tropsch synthesis. It is well established that at constant temperature adding alkali promoter to Fischer Tropsch synthesis catalysts like Fe, Co or Ru (2) decreases the rate of reaction while increasing the alkene/alkane ratio. As discussed earlier a number of theories have been proposed to explain these observations. The $^1$H NMR and microcalorimetric results done here indicate that adding even small amounts of K promoter affects the hydrogen chemisorption properties of Ru/SiO$_2$. In the presence of K there is reduction in the mobility and availability of atomic hydrogen with intermediate and low heats of adsorption. Thus, the reduction of hydrogen on the catalyst surface causes a decreases in the amount of alkane which is produced as chain termination via hydrogenation of the unsaturated carbon chain is decreased. This gives a qualitative explanation for the increase in the alkene to alkane ratio observed in the presence of alkali promoters. Further, hydrogen being a reactant in the process, lower concentrations of hydrogen implies that the overall rate of reaction
has to decrease if Langmuir-Hinshelwood or power law kinetics are assumed for Fischer Tropsch synthesis.

Adding K to Ru/SiO₂ reduces the amounts of hydrogen adsorbed and greatly suppresses the weakly bound state observed on unpromoted Ru/SiO₂ at higher pressures. It is speculated that the state observed at high pressures consists of mobile, atomic hydrogen which has a greater propensity to react than the strongly bound atomic hydrogen observed at lower pressures. The above observations increase our fundamental understanding of the role of K additives and their interaction with hydrogen at high pressures in commercial processes, which are also operated at higher pressure and temperature. For example, the observation that K addition suppresses the amount of hydrogen adsorbed has an important bearing on all chemical reactions in which hydrogenation is involved. Fischer-Tropsch synthesis is an example of a reaction where alkali additives are used and hydrogenation plays an important role.

Conclusions

In this work microcalorimetry and proton NMR have been combined to elucidate the interaction of hydrogen with Ru/SiO₂ and the effect K addition has on the energetics and kinetics of this process. The weakly bound hydrogen observed at high pressures as well as intermediate adsorption states with heat of adsorption between 10 and 50 kJ/mole are greatly reduced upon addition of K to
Ru/SiO₂. The initial differential heat of adsorption are similar on K/Ru/SiO₂ and Ru/SiO₂ suggesting that there is no electronic effect influencing hydrogen chemisorption. This conclusion is also corroborated by the invariance of the Knight shift in proton NMR studies on K/Ru/SiO₂ which indicated that there is no through-metal electronic interaction between adsorbed hydrogen and the added K.

There is reduction in amounts of hydrogen adsorbed on Ru particles as well as of hydrogen spilled over to the silica support upon addition of potassium to Ru/SiO₂ catalysts. This was explained by postulating that K blocks the edge and corners sites and thus, reducing the hydrogen adsorption-desorption capacity of the catalyst. A reduction in hydrogen mobility was also observed upon adding large amounts of K to Ru/SiO₂ catalysts and this could be relevant to the mechanism of hydrogenation reactions such as Fischer-Tropsch synthesis.

Acknowledgments

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References


### Table 1
Catalyst characteristics

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<th>Catalyst</th>
<th>$H/Ru_{\text{surface}}$</th>
<th>$H/Ru_{\text{surface}}^{1\text{H NMR}}$</th>
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<tr>
<td>4% Ru/SiO$_2$</td>
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<td>0.087</td>
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<tr>
<td>4% Ru 50 at.% K/SiO$_2$</td>
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</table>
**Figure Captions**

Figure A1. Heats of adsorption of hydrogen as a function of hydrogen coverage (H/Rusurface) for Ru and K/Ru catalysts with 6, 33 and 50 atomic % K.

Figure A2. H/Rusurface ratio as determined from $^1$H NMR spectra against $H_2$ pressure for Ru catalyst and K/Ru catalysts containing 6 and 66 atomic % K.

Figure A3. (a) single pulse and (b) selective excitation $^1$H NMR spectra for K/Ru catalyst with 6 atomic % K, at 7 Torr $H_2$.

Figure A4. (a) single pulse and (b) selective excitation $^1$H NMR spectra for K/Ru catalyst with 66 atomic % K, at 7 Torr $H_2$.

Figure A5. Variation of Knight shift with hydrogen pressure for K/Ru catalyst with 6 atomic % K.

Figure A6. Variation of Knight shift with hydrogen pressure for K/Ru catalyst with 66 atomic % K.

Figure A7. Selective excitation $^1$H NMR spectra at various temperatures for K/Ru catalyst with 6 atomic % K and corresponding simulated spectra with various values of exchange parameter $k_{ex}$.

Figure A8. Arrhenius type plot of $k_{ex}$ versus 1000/T for K/Ru catalyst with 6 at% K.
Figure A9. Heats of adsorption of H₂ and H/Ru$_{\text{surface}}$ determined volumetrically and by $^1$H NMR as a function of hydrogen pressure for Ru/SiO$_2$ catalyst and K/Ru/SiO$_2$ catalysts with 6, 33 and 50 atomic % K.
Figure A2.
Figure A3.

7 Torr H₂
Figure A4.
Figure A5.
Figure A6.
Figure A7.
Coverage = $H/R_u = 0.4$

Slope = $-E/R = -4570.4$

$E_{des} = 38 \text{ kJ/mole}$

1000/T (K⁻¹)

Figure A8.
Figure A9.
APPENDIX B

SURFACE COMPOSITIONS OF Pt-Rh/Al₂O₃ CATALYSTS BY
\(^{129}\text{Xe}\) NMR SPECTROSCOPY

Introduction

\(^{129}\text{Xe}\) NMR spectroscopy has been widely used to study zeolites. This technique was originally introduced by Ito and Fraissard (1) who showed that \(^{129}\text{Xe}\) NMR can be used to probe void volume, dimensions of channels and cavities, short distance crystallinity, acidity of zeolites as well as to study effects of cations, metal particles and chemisorption of gases like H₂ and CO on zeolite structure. de Menorval et al. (2) reported that this technique was useful in determining the number of metal particles inside the Pt/NaY zeolite cages. \(^{129}\text{Xe}\) is a nucleus suitable for NMR studies because, (i) It has a nuclear spin \(I=1/2\). (ii) It is chemically inert (non-reactive). (iii) It has high natural abundance (26.44%) (iv) It has a large, spherical electron cloud which is perturbed by physical interactions with other species or surfaces.

The chemical shift of \(^{129}\text{Xe}\) interacting with a supported catalyst depends on various factors such as collisions between xenon atoms in the gas phase as well as the collisions with the channel walls of the support, local electric fields (when \(C^{2+}\) cations are present) and local magnetic fields (when paramagnetic species are present) [Jameson et al. (3), Ito and Fraissard (1)]. For zeolites of the type NaYₓ, the chemical shift of \(^{129}\text{Xe}\) increases linearly with xenon concentration or pressure.
At very low xenon concentration, probability of Xe-Xe collisions is very small and motion of xenon atoms is disturbed only by cage walls. So the chemical shift, $\delta_s = 58 \pm 2$ ppm obtained by extrapolating the $\delta = f[Xe]$ line to $[Xe]=0$, can be considered as the characteristic of the zeolite with respect to xenon interaction.

Ahn et al. (4) have characterized Pt-Cu/NaY catalysts using $^{129}$Xe NMR and EXAFS (extended X-ray absorption fine structure). The authors suggested that for the Pt-Cu bimetallic catalysts, the chemical shift of xenon was given by an expression,

$$\delta = \left( \delta_{Pt} n_{Pt} + \delta_{Cu} n_{Cu} + \delta_{sup} n_{sup} \right) / n$$  \[1\]

where $n = n_{Pt} + n_{Cu} + n_{sup}$  \[2\]

where $n_{Pt}$, $n_{Cu}$ and $n_{sup}$ are the number of xenon atoms adsorbed on Pt clusters, Cu clusters and NaY zeolite, respectively and $\delta_{sup}$ is the chemical shift of adsorbed xenon on pure NaY zeolite at the same xenon pressure as used for Pt/NaY. The authors proposed that oxygen, when chemisorbed on metallic surfaces, prohibited xenon adsorption. Hence the values of $n_{sup}$ and $n_{Pt}$ could be obtained from a xenon adsorption isotherm obtained after and before oxygen chemisorption, respectively.

Yang et al. (5) studied Pt-Ir bimetallic catalysts supported on NaY zeolite using $^{129}$Xe NMR and ethane hydrogenolysis. They observed only one NMR peak for Pt-Ir/NaY bimetallic catalysts which implied fast exchange of xenon either between closely separated monometallic clusters of Pt and Ir or on bimetallic Pt-Ir clusters. Based on the non-linear decrease in the Xe chemical shift with
increasing Ir content, the authors claimed that bimetallic Pt-Ir clusters were formed.

Very few studies have applied the $^{129}$Xe NMR technique to supported metal catalysts. Boudart et al. (6) studied the progressive penetration of adsorbates such as hydrogen and oxygen into Pt/$\gamma$-Al$_2$O$_3$ catalyst with this technique. Valenca and Boudart (7) also studied the competition between diffusion and reaction (or chemisorption) within platinum catalyst pellets with adsorbed H$_2$ and O$_2$ using $^{129}$Xe NMR. They observed two distinct NMR lines under certain conditions which meant that xenon encountered two different environments as the surface reaction proceeded slowly into the pellets and the adsorption front was sharp. They observed a single NMR line under certain other conditions, which was due to single environment encountered by xenon atoms and the adsorption front being "fuzzy".

Filiminova et al. (8) using $^{129}$Xe NMR characterized two Pt/$\gamma$-Al$_2$O$_3$ catalysts- Pt-I catalysts prepared from a precursor (I) containing chloride ions-H$_2$PtCl$_6$ and Pt-II catalysts prepared from a precursor (II) not containing chloride ions-[Pt(CO)$_2$$_n$ complex in acetone solution. Pt-II catalysts contained platinum only in the zero oxidation state- Pt$^0$, whereas Pt-I catalysts contained platinum in zero (Pt$^0$) and +2 oxidation state (Pt$^{+2}$). From their results, the authors deduced that the affinity of xenon towards Pt$^{+2}$ was weaker than that towards Pt$^0$, possibly
due to shielding of Pt$^{2+}$ ions by Cl$^{-}$ ions. This indicated that platinum is more accessible to xenon atoms in Pt-II catalysts than in Pt-I catalysts.

Cheung (9) studied amorphous materials such as silica and alumina by $^{129}$Xe NMR at 144 K. He observed narrow resonance lines even for such amorphous materials which indicated rapid motion of xenon atoms among micropores. A parabolic dependence of the chemical shift on xenon density in the low xenon loading regime for silica, alumina and their mixtures was explained in terms of a distribution of micropore sizes.

From the literature review it can be seen that it is possible to study the surfaces of supported catalysts using $^{129}$Xe NMR spectroscopy. Since xenon undergoes only weak, physical interactions with supported catalysts, the surfaces of bimetallic catalysts will not be altered in the presence of xenon. Hence our objective was to determine the surface compositions of adsorbate-free Pt-Rh/Al$_2$O$_3$ catalysts by this method.

**Methods**

(a) **Catalyst Preparation**

One platinum and one rhodium catalyst, each with a metal loading of 3 wt% and supported on γ-alumina (Johnson Matthey, BET surface area=100 m$^2$/g) were prepared by incipient wetness impregnation method using H$_2$PtCl$_6$·6H$_2$O and Rh(NO$_3$)$_3$·2H$_2$O (AESAR) as precursors. Appropriate amounts
of the metal salts were dissolved in deionized water and a measured amount of the alumina support was added to the solution. The resulting slurry was dried at room temperature for 20 hours and then at 393 K for 8 hours. Three Pt–Rh bimetallic catalysts with metal loadings of 3% Pt –1% Rh, 3% Pt – 3% Rh and 1% Pt – 3% Rh were prepared in a similar manner via co-impregnation. All of the catalysts were reduced in flowing hydrogen at 673 K and subsequently washed with hot deionized water to remove residual chloride. Selective hydrogen chemisorption was used to measure the dispersion of the monometallic as well as the bimetallic catalysts.

(b) Preparation of NMR samples

The NMR tubes of 10 mm O.D. were filled with about 1.4 g of catalyst sample and attached to the sample ports of an adsorption apparatus described elsewhere. Subsequently, 760 Torr of helium was introduced into the manifold and the samples were heated to 393 K for 15 min., then evacuated and dosed with 760 Torr of hydrogen. The samples were then reduced at 673 K for 2 hours introducing fresh hydrogen every 30 min. Then the samples were evacuated at 573 K overnight and cooled to room temperature. Each sample was dosed with about 600 Torr of xenon gas and was allowed to equilibrate for about 1 hr. Finally the samples were immersed in a liquid nitrogen bath to ensure that all the xenon condensed in the sample tube. The samples were sealed with an oxy-acetylene microtorch maintaining them in the liquid nitrogen bath and then weighed. The
net weight of the catalyst sample was obtained by subtracting the weight of the empty tube from the final weight of the sealed sample. The NMR experiments were carried out in a home built NMR spectrometer with a proton resonance frequency of 250 MHz. The resonance frequency for $^{129}$Xe nucleus was 69 MHz in this magnetic field. Typically, 7200 scans with a repetition time of 0.5 s were taken, but sometimes larger number of scans were required to improve the signal to noise ratio.

**Results and Discussion**

The NMR lines actually observed on all the catalysts were much broader than expected (peak width: 4 to 6 kHz) which could be due to exchange broadening as a result of fast exchange of xenon trapped in micropores and mesopores or macropores. The peak at 0 ppm (Figs. B1, B2) is due to xenon-xenon interactions in the gas phase and this is the primary reference for shifts in all $^{129}$Xe NMR spectra. The NMR line on Rh/Al$_2$O$_3$ catalyst is difficult to see but it was more easily visible at higher temperatures (Fig. B2). The peak corresponding to xenon interaction with Rh particles shifted toward the upfield direction (closer to the peak due to gas phase xenon) with increasing temperature. This is most likely due to increased exchange of xenon on Rh particles with the gas phase xenon. The spectrum for alumina support with corresponding $^{129}$Xe chemical shift is shown in Fig. B3. A variation in chemical shifts was observed on the Pt-Rh bimetallic
catalysts as the overall composition changed from 0% Rh (pure Pt) to 100% Rh (pure Rh) can be seen (Fig.B1). Since we observed single line in NMR spectra, we deduced that xenon atoms must be undergoing fast exchange over platinum, rhodium and alumina sites. This fact was utilized to calculate the surface compositions of Pt-Rh bimetallic catalysts once the chemical shifts of $^{129}$Xe on pure alumina and pure Pt and pure Rh particles were known. For Pt/Al$_2$O$_3$ catalyst, the chemical shift was expressed as,

$$\delta_{Pt/Al_2O_3} = \delta_{Pt} X_{Pt} + \delta_{Al_2O_3} X_{Al_2O_3}$$

where $X_{Pt}$ and $X_{Al_2O_3}$ were the fractions of total area occupied by Pt particles and alumina support per gram of catalyst. These were calculated as follows,

$$X_{Pt} = (f_{w,Pt}/M_{w,Pt}) \cdot N_0 \cdot D \cdot (4\pi r_{Pt}^2)/S_{BET}$$

and $$X_{Al_2O_3} = 1 - X_{Pt}$$

where $f_{w,Pt}$ is the weight fraction, $M_{w,Pt}$ is the molecular weight and $r_{Pt}$ is the atomic radius of platinum respectively; $D$ is the dispersion of the catalyst, $N_0$ is the Avogadro's number and $S_{BET}$ is the BET surface area of the catalyst. Thus from this expression, we calculated the chemical shift $\delta_{Pt}$ of pure platinum particles after knowing the xenon chemical shifts for pure alumina support and alumina supported platinum catalyst for the same xenon pressure. Similar expressions were written to calculate the shift $\delta_{Rh}$ of pure rhodium particles. For Pt-Rh bimetallic catalysts supported on alumina, expression analogous to [3] was written as,
\[ \delta_{\text{Pt-Rh/Al}_2\text{O}_3} = \delta_{\text{Pt}} \cdot X_{\text{Pt}} + \delta_{\text{Rh}} \cdot X_{\text{Rh}} + \delta_{\text{Al}_2\text{O}_3} \cdot X_{\text{Al}_2\text{O}_3} \]  

.....[6]

The sum \((X_{\text{Pt}} + X_{\text{Rh}})\) was calculated from an expression similar to equation (4) and the fraction \(X_{\text{Al}_2\text{O}_3}\) was found from the relation,

\[ X_{\text{Al}_2\text{O}_3} = 1 - (X_{\text{Pt}} + X_{\text{Rh}}) \]  

.....[7]

Thus the fraction \(X_{\text{Rh}}\) was calculated from equation [6] since all the chemical shifts in that equation are known. Then the surface mole fraction of Rh, \(X_{\text{Rh}}^s\) can be computed easily as follows,

\[ X_{\text{Rh}}^s = \frac{X_{\text{Rh}}}{(X_{\text{Pt}} + X_{\text{Rh}})} \]  

.....[8]

The surface compositions estimated from this procedure and shown in Fig. B4 suggest that platinum segregates to the surface of Pt-Rh bimetallic catalysts which are not influenced by any adsorbate. This result is in agreement with the atomistic simulations performed at 304 K for particles with a dispersion of 31% and in the absence of any adsorbate (see Fig. B4). Segregation of Pt to the adsorbate-free surface of Pt-Rh bimetallic catalysts has been reported in many previous theoretical and experimental studies.

**Conclusions**

The surface compositions of alumina supported Pt-Rh catalysts were determined in the absence of adsorbates using \(^{129}\text{Xe}\) NMR spectroscopy. The surface was found to be enriched in platinum in the absence of adsorbates. This is in agreement with previous theoretical and experimental studies. Thus \(^{129}\text{Xe}\)
NMR appears to be a useful, non-destructive method to examine the surfaces of supported bimetallic catalysts not influenced by chemisorption induced surface segregation.

References

Figure B1. $^{129}\text{Xe}$ NMR Spectra at 600 Torr Xe for alumina supported Pt, Rh and Pt-Rh catalysts.
Figure B2. $^{129}$Xe NMR Spectra for 3% Rh/Al$_2$O$_3$ catalyst with 600 Torr Xenon at various temperatures.
Figure B3. $^{129}$Xe NMR spectrum for Al$_2$O$_3$ support
Figure B4. Surface compositions of Pt-Rh/Al₂O₃ catalysts in the absence of adsorbates
The $^1$H NMR spectra of silica or alumina supported transition metal catalysts show at least two distinct resonances. The downfield diamagnetic resonance arises due to the hydroxyl groups of the support as well as hydrogen spilled over from metal particles on to the support. The upfield paramagnetic resonance arises due to the hyperfine interaction of conduction electrons of the metal with the probe nuclei, that is, $^1$H spins. This second resonance corresponds to hydrogen adsorbed on the metal particles. However, this does not represent hydrogen on metal surface alone but represents hydrogen in the gas phase too because it is in fast exchange with the hydrogen on metal surface, on the NMR time scale under high pressure conditions (hydrogen pressure > 100 Torr). Hence the contribution from gas phase hydrogen to this resonance needs to be separated in order to accurately quantify the hydrogen on metal surface. This is shown here with the example of a 4% Ru/SiO$_2$ catalyst. In this work, it was observed that when CO was adsorbed on the surface of this catalyst at room temperature, it completely displaced the hydrogen on Ru surface as the upfield H/Ru resonance was not visible after CO adsorption (Fig. C1). When large amounts of hydrogen were adsorbed on the CO covered Ru surface, a narrow peak superimposed with the downfield peak of the support, was visible. This represented the gas phase
hydrogen which could be easily quantified by deconvoluting the peaks. This is shown in Fig. C2 for two high values of hydrogen pressure. The amount of gas phase hydrogen per surface ruthenium site \( \frac{H_{\text{gas}}}{\text{Ru}_{\text{surface}}} \) was also calculated from ideal gas law at various pressures, assuming that hydrogen behaves as an ideal gas. These values agree quite well with those calculated experimentally as shown in Fig. C2. This calculation based on ideal gas law is illustrated below.

(a) Diameter of NMR tube, \( d = 0.5 \text{ cm} \); length \( L = 2.54 \text{ cm} \)

Porosity of catalyst \( \varepsilon = 0.76 \); Temperature \( T = 400 \text{ K} \)

Universal gas constant \( R = 82.06 \text{ cm}^3\text{-atm/gmole-K} \)

Avogadro's number \( N_0 = 6.024 \times 10^{23} \text{ molecules/gmole} \)

Molecular weight of ruthenium \( M_w = 101 \text{ g/gmole} \)

(b) Volume of NMR tube \( V = \frac{\pi}{4}d^2L = 0.4987 \text{ cm}^3 \)

Volume of gas phase hydrogen in the tube \( V_g = \varepsilon V = (0.76)(0.4987) = 0.379 \text{ cm}^3 \)

Ideal gas law; \( PV_g = n_gRT \) or number of moles of hydrogen gas,

\[ n_g = \frac{PV_g}{RT} = \frac{(P/760)(0.379)/(82.06 \times 400)}{1.519 \times 10^{-8} P}, \]

where \( P \) is pressure in Torr

Number of molecules of hydrogen gas \( N_g = n_g N_0 = 9.153 \times 10^{15} P \).

At \( P = 100 \text{ Torr} \), \( N_g = 9.153 \times 10^{17} \)

(c) Typical weight of catalyst in NMR tube \( w = 0.14 \text{ g} \)

Weight loading of Ru catalyst \( w_1 = 4\% \)

Total number of Ru atoms in the NMR sample,
\[ \text{N}_{\text{Ru, total}} = w \times w_1 \times \frac{N_0}{M_w} = (0.14)(0.04)(6.024 \times 10^{23}) / (101) \]

\[ \text{N}_{\text{Ru, total}} = 3.37 \times 10^{19} \]

Catalyst dispersion \( D = 8.7\% \)

Number of surface Ru atoms in the NMR sample,

\[ \text{N}_{\text{Ru, surface}} = \text{N}_{\text{Ru, total}} \times D = 2.93 \times 10^{18} \]

Hence, number of molecules of gas phase hydrogen per surface ruthenium site,

\[ \frac{H_{\text{gas}}}{R_{\text{u, surface}}} = \frac{N_g}{N_{\text{Ru, surface}}} = \frac{9.153 \times 10^{17}}{(2.93 \times 10^{18})} \]

\[ \frac{H_{\text{gas}}}{R_{\text{u, surface}}} = 0.312 \text{ at 100 Torr H}_2 \text{ for 4\% Ru/SiO}_2 \text{ catalyst with 8.7\% dispersion}. \]
Figure C1. $^1$H NMR spectra of 4% Ru/SiO$_2$ catalyst with (a) 680 Torr H$_2$ and (b) 200 Torr H$_2$ after saturating the surface with CO.
Figure C2. Estimation of gas phase hydrogen from ideal gas law (solid line) and experimentally after saturating the surface with CO (diamonds)
APPENDIX D

NATURE OF ADSORBED HYDROGEN ON Ru/SiO₂

Two peaks, termed as α and β, were observed by Bhatia et al. (1) corresponding to hydrogen adsorbed on Ru/SiO₂ catalysts. It was confirmed that the hydrogen species represented by the α peak corresponded to a strongly bound hydrogen on the surface of Ru metal particles and was speculated to occupy the three fold hollow sites. However, the exact nature and location of the hydrogen species represented by the β peak is not still clear. It is known that this peak appears only at H₂ pressures above 100 Torr and corresponds to a weakly bound species. The possible explanations for the nature and location of this species are discussed below based on some experimental results and elementary calculations.

From the data on pore size distribution, it was found that silica support has a bimodal pore distribution with mean pore diameters of 100 Å (10⁻⁶ cm) and 10⁵Å (10⁻³ cm). The average diameter of ruthenium particles is less than 100 Å and most of these particles will reside inside such micropores. A time scale of 700 μs is used in the following calculations because Engelke et al. (2) from two dimensional ¹H NMR observed that the hydrogen corresponding to α and β peaks was in slow exchange with a time scale of 700 μs.
(a) Mean free path of hydrogen

It is given by the following expression (3):

$$\lambda = \left[ 1.41 \sigma^2 n^* \right]^{-1}$$

where $\sigma$ = molecular diameter in cm and

$$n^* = \text{no. of molecules per cm}^2 = \left[ \frac{P N_0}{RT} \right]$$

$$\lambda = 2.24 \times 10^{-6} \left( \frac{T}{P} \right)$$

Atomic radius of H atom = 0.37 Å, hence $\sigma = 0.74 \times 10^{-8}$ cm

At $T = 300$ K, $P = 1$ atm, $\lambda = 6.64 \times 10^{-4}$ cm

$$P = 0.132 \text{ atm (100 Torr), } \lambda = 5.1 \times 10^{-3} \text{ cm}$$

$$P = 0.0132 \text{ atm (10 Torr), } \lambda = 5.1 \times 10^{-2} \text{ cm}$$

Depending on the pore diameter and mean free path of hydrogen at a given pressure, the diffusion of hydrogen could be either molecular type or Knudsen type. At $P = 100$ Torr,

For small pores, $d / \lambda = 1.95 \times 10^{-4} << 0.2$, hence Knudsen diffusion

For large pores, $d / \lambda = 0.196$ could be molecular diffusion or in transition region.

(b) Molecular diffusion

Diffusion coefficient of hydrogen in gas phase is given by the following empirical correlation (4):

$$D_{H2} = \left[ 10^{-3} T^{1.75} \left( \frac{M_A + M_B}{M_AM_B} \right) \right] / \left[ P \left( \Sigma v_A \right)^{1/3} + \left( \Sigma v_B \right)^{1/3} \right]$$
For $H_2$, $v_A = v_B = 3.96$, $M_A = M_B = 2$.

Hence $D_{H_2} = 3.16 \times 10^{-4} \left( \frac{T^{1.75}}{P} \right)$

At $T = 300$ K and $P = 1$ atm, $D_{H_2} = 6.84 \text{ cm}^2/\text{s}$

(c) Knudsen diffusion

The coefficient of Knudsen diffusion is given by the following expression (5)

$$D_K = \frac{2d}{3} \left( \frac{8RT}{\pi M} \right)^{1/2}$$

$R = 8.314 \times 10^7 \text{ erg/gmole K}$, $M = 2$ for hydrogen

At $T = 300$ K, $D_K = 1.188 \times 10^5 d$

(i) For small pores, $d = 10^{-6}$ cm, $D_K = 0.1188 \text{ cm}^2/\text{s}$

$$L^2 = D \tau,$$

For $\tau = 700 \mu s$, $L = 9.1 \times 10^{-3}$ cm

Thus the diffusional distance traveled by hydrogen is 1000 times the average pore diameter and hence hydrogen representing $\alpha$ and $\beta$ peaks will be in fast exchange.

(ii) For large pores, $d = 10^{-3}$ cm, $D_K = 1.188 \times 10^2 \text{ cm}^2/\text{s}$

Thus $D_K >> D_{H_2}$ and hence diffusion will be molecular..

Diffusional distance traveled by hydrogen in gas phase,

$$L^2 = D \tau \quad \text{(based on Fick's law of diffusion)}$$

For $\tau = 700 \mu s$, $L = 0.069 \text{ cm} = 6.9 \times 10^6 \text{Å}$
Pore diameter for large pores is 0.001 cm and the diffusional distance traveled is 70 times the average pore diameter. Hence hydrogen representing α and β peaks will be in fast exchange with each other even within the large pores.

(d) Surface Diffusion coefficient of hydrogen

\[ D_s = (\lambda/4) \left( kT/2\pi m \right)^{1/2} \]

\[ m=1, k = 1.38 \times 10^{-16} \text{ erg} / K \]

At \( T = 300 \text{ K} \) and \( P = 1 \text{ atm} \), \( \lambda = 6.64 \times 10^{-4} \text{ cm} \)

\[ D_s = 1.34 \times 10^{-11} \text{ cm}^2/\text{s} \]

If \( L^2 = D_s \tau \) then, for \( \tau = 700 \mu s \), \( L = 9.6 \times 10^{-8} \text{ cm} = 9.6 \text{ Å} \)

If surface diffusion is the prevalent mechanism for hydrogen to diffuse then it is possible that hydrogen representing α and β peaks will be in slow exchange with each other. However, it was shown by Engelke et al.(2) that surface diffusion is not the dominant mechanism of hydrogen mobility.

Possible explanations for β state

(a) Effects of different pore sizes

The α and β states could correspond to hydrogen residing in the small and large pores respectively. It was shown above that Knudsen diffusion prevails in the smaller micropores whereas molecular hydrogen diffusion is dominant in the larger mesopores and macropores. However, diffusional distance of hydrogen is quite large over the NMR time scale for both, small and large pores, whichever
be the diffusion mechanism. Hence if hydrogen corresponding to $\alpha$ and $\beta$ peaks represents hydrogen residing in small and large pores then there has to be fast exchange between these two species which not true. Hence these two forms of hydrogen ($\alpha$ and $\beta$) can not correspond to hydrogen residing in small and large pores.

(b) Surface species or spillover to support

It could be some species formed by surface diffusion since it is a slow process and could explain the lack of fast exchange between $\alpha$ and $\beta$ states. However if it is a species which spills over to the support, the following questions are still unanswered. Why does it show large Knight shifts? and How is it different from spilled over hydrogen observed close to hydroxyl group resonance?

(c) Precursor state

$\beta$ state could be a molecular precursor to $\alpha$ state as it can be a weakly bound species. The dissociation process could be intrinsically slow thus explaining the slow exchange between the two species. A precursor state can exist over an occupied site (Xu and Koel (6)). If there is any correlation between appearance of $\beta$ state and higher mobility of $\alpha$ state then it can be explained only by such precursor state. But in such a case, reduction in population should cause a reduction in $\alpha$ population too. One more possibility is that $\beta$ state could be just a weakly bound species which appears only at higher pressures and is independent of the existence of $\alpha$ state.
References


APPENDIX E

INTERACTION OF H₂ AND CO ON Ru/SiO₂

Introduction

Several research efforts have been concentrated on the study of Fischer-Tropsch reaction for coal liquefaction because liquid fuels are cheaper and more efficient in many ways than solid or gaseous fuels. Hydrogenation of carbon monoxide over supported metal catalysts has also been studied extensively because this is the first step in the production of liquid hydrocarbon fuels by Fischer-Tropsch synthesis. On industrial scale, iron and cobalt are used as catalysts for Fischer-Tropsch synthesis (1). For academic research, ruthenium is used because it gives much simpler products consisting of linear olefins, paraffins and relatively few oxygenated products and it does not form bulk carbide like iron and cobalt do, under reaction conditions (2).

Originally Fischer and Tropsch (3) assumed metal carbides to be the reaction intermediates. This was contradicted by Kummer et al. (4) who proposed that oxygen containing surface complexes such as CHO(ads) or HCHO(ads) were reaction intermediates and this was supported by the work of Dalla Betta et al. (5) and Vannice (6) on Ru catalysts. However, more recent studies by Ekerdt and Bell (7) and Biloen et al. (8) on Ru catalysts have supported the hypothesis that surface carbon atoms, generated by dissociation of
CO are the actual reaction intermediates. This surface carbon is hydrogenated to produce adsorbed methylene and methyl groups and it is proposed that the methyl groups act as precursors for the formation of methane as well as for the growth of hydrocarbon chains. This has also been supported by the work of Brady and Petit (9) who showed that a spectrum of hydrocarbons can be formed by the reaction of \( \text{CH}_2\text{N}_2 \) and \( \text{H}_2 \) over Ru and other Group VIII metals. Ekerdt and Bell (7) also suggested that hydrogenation of surface carbon atoms can occur even after the elimination of chemisorbed CO from the surface. Although Dalla Betta and Shelef (10) have proposed that CO dissociation is the rate controlling step for CO hydrogenation, Biloen et al. (8) showed using isotopic tracer studies that CO dissociation is very rapid on Ru and unlikely to be the rate limiting process. Biloen et al. (8) proposed that the conversion of \( \text{C}_1 \) species to \( \text{C}_2 \) species was rate controlling and Kobori et al. (11) have supported this proposal by mechanistic study of CO hydrogenation over Ru/SiO\(_2\) and Ru black.

In this study, we have examined the interaction of CO and \( \text{H}_2 \) on Ru/SiO\(_2\) catalyst by \( ^1\text{H} \) NMR. Since NMR is a quantitative method, surface coverage of adsorbed hydrogen and hydrocarbon species can be directly measured. Based on this, the surface coverage of CO can also be deduced. The objective was to examine the kinetics of CO hydrogenation and determine the reaction orders with respect to coverage of surface species. The rate constants and activation energy was also determined from this study and compared with previous studies.
Methods

The Ru/SiO₂ catalyst was prepared according a method described elsewhere (12). The catalyst was reduced in hydrogen for 1.5 hrs at 673 K dosing fresh hydrogen every 30 min. The sample was cooled to room temperature and reaction of hydrogen with CO on Ru/SiO₂ catalysts was monitored via ¹H NMR spectroscopy. The catalyst sample was dosed with about 50 Torr CO at room temperature and allowed to equilibrate for an hour. The CO was then evacuated for 30 min. at room temperature and heating was started after stopping the evacuation. After a certain desirable temperature was reached, hydrogen was dosed at a pressure of about 460 Torr and the kinetics of the reaction was monitored via ¹H NMR spectroscopy by recording the spectra at various time intervals.

Results and Discussion

Two peaks were seen due to H/Ru on the catalyst at all times in the NMR spectra although they were not apparent in the beginning (Fig. E1). These peaks were labeled as α and β resonances (12). Quantification of the spectra yielded the values of H/Ru_{surface} with time, for both α and β peaks (Fig. E2). It is known that the α resonance is associated with hydrogen adsorbed on the surface
of ruthenium particles. Hence this peak was considered as a measure of the surface coverage of CO and the CO coverage was calculated as follows:

\[
[\text{CO/Ru}_{\text{surf}}] = [1 - \{ (\text{H/Ru}_{\text{surf}})/(\text{H/Ru}_{\text{surf}})_{\text{sat}}\}]
\]

If the reaction kinetics is such that the reaction is first order in CO surface coverage and zero order in H\(_2\) surface coverage then we can write,

\[
\frac{\text{d}\theta_{\text{CO}}}{\text{d}t} = k\theta_{\text{CO}}
\]

where \(k\) is the rate constant for the reaction and \(\theta_{\text{CO}}\) is the surface coverage of CO. Upon integrating this equation, it can be seen that a plot of \(\ln([\text{CO}]/[\text{CO}]_{\text{initial}})\) versus time would be a straight line with a slope equal to the rate constant \(k\). Such a plot was indeed found to be a straight line and value of \(k\) was obtained from this plot (Fig. E3). The rate constants obtained are in the range of \(10^{-3}\) to \(10^{-4}\) s\(^{-1}\) which is comparable to the range of \(10^{-2}\) to \(10^{-4}\) s\(^{-1}\) reported by Dautzenberg et al. (13) but much smaller than the range of about 0.1 to 1 s\(^{-1}\) reported by Komaya et al. (14).

The reaction was carried out at different temperatures and the quantities mentioned above were plotted to obtain values of \(k\) as a function of temperature. An Arrhenius plot of \(\ln(k)\) versus \(1/T\) yielded a value of 54 kJ/mole for activation energy (Fig. E4). This value appears to be much lower than a value of about 100 kJ/mole reported for the activation energy of CO hydrogenation reaction on Ru catalysts (5-7). Further, Ekerdt and Bell (7) observed reaction order of \(-0.6\) with respect to CO partial pressure and of 1.5 with respect to H\(_2\) partial pressure,
consistent with the results of Vannice (6). However, we are assuming an order of 1 with respect to surface coverage of CO and an order of zero with respect to surface coverage of hydrogen. This is consistent with the hypothesis of Dalla Betta (5) et al. that CO dissociation is the rate controlling step. However, it is in contradiction to the hypothesis of Ekerdt and Bell (7) and Biloen et al. (8) who proposed that the hydrogenation of $C_1$ species to $C_2$ species is the rate limiting step.

The main products observed by Ekerdt and Bell (7) were methane, ethane, propane and propylene. However, it needs to be clarified in our case whether CO and hydrogen are actually reacting on Ru surface. Although Kobori et al. (11) report that the surface hydrocarbon species occupy only a small fraction of Ru surface as most of the surface is covered with adsorbed CO, large amounts of hydrocarbons desorbing from the surface are expected to be present in the gas phase. However, peaks corresponding to gas phase products such as methane or water are not seen in our $^1$H NMR spectra. Hence formation of products needs to be investigated via other techniques such as mass spectrometry or IR spectroscopy.

The reaction may not be occurring because CO might be desorbing from the surface at higher temperatures. The following experiment was carried out to check this possibility. At room temperature, even though hydrogen was dosed on a surface saturated with CO, peaks due to H/Ru were not seen even after
waiting for long time intervals which suggested that hydrogen was not able to
displace CO adsorbed on Ru surface at room temperature. This was also
observed at 400 K by doing the following experiment. The CO on Ru surface was
allowed to equilibrate and then evacuate at room temperature. The temperature
was then raised to 400 K and maintained for 1 hour without any exposure to
hydrogen. Then the sample was cooled back to room temperature and hydrogen
was dosed at 460 Torr. Again H/Ru peaks could not be seen which suggested
that CO did not desorb from Ru surface at 400 K.

The other possibility is that hydrogen is assisting CO desorption at higher
temperatures. In that case, we are measuring the kinetics of CO desorption
instead of reaction kinetics. Gland et al. (15) observed that chemisorbed CO was
displaced from the surfaces of Ni(100) and Pt(111) by hydrogen in the range of
309 to 328 K. Adsorbed CO was removed about 5 times faster in the presence of
hydrogen than in the absence of hydrogen which suggested that displacement of
CO was occurring in the presence of hydrogen. The thermal activation energies
for the displacement process were found to be in the rage of 8 to 12 kcal/mol.
The displacement rates were first order in CO suggesting that single adsorbed
CO molecule was involved in the rate-limiting step. Displacement of adsorbed
CO by hydrogen was also observed by Zhang and Gellman (16) on Ni(111)
surface in the hydrogen pressure range of 10^{-9} to 10 Torr. They reported a net
decrease in the CO desorption energy from 30 kcal/mol in ultrahigh vacuum to
22 kcal/mol in the presence of hydrogen. The influence of hydrogen on the CO desorption kinetics could be due to a shift of CO molecules from linear to bridging sites in the presence of hydrogen. The initial (zero coverage) heat of adsorption of CO on Ru/C at 423 K is reported to be 138 kJ/mol according to calorimetric measurements (17) which is much higher than the value of 54 kJ/mole obtained in this work. However, the heat of adsorption is a strong function of coverage. For Pt/SiO₂ catalysts, the heat of adsorption of CO varies from 150 to 10 kJ/mole as the coverage varies from 0 to 0.4, at 390 K (17). Since the CO coverage is varying from 1 to 0 in our case, we might be observing the heat of adsorption averaged over the entire range of coverages.

Conclusions

It needs to be confirmed whether CO and H₂ are reacting on the surface of Ru/SiO₂ since peaks due to products such as gas phase methane and water are not seen in the ¹H NMR spectra. If there is a reaction occurring, it appears to be first order in CO surface coverage and zeroth order in H₂ surface coverage.

References


Figure E1. $^1$H NMR spectra for reaction of $\text{H}_2$ with $\text{CO}$ at various time intervals
Figure E2. A logarithmic plot of normalized CO concentration with time.
Figure E3. Kinetics of CO hydrogenation reaction on Ru/\text{SiO}_2.

\[ k = 0.02461 \text{ min}^{-1}, \ T = 400 \text{ K} \]
\[ k = 0.1168 \text{ min}^{-1}, \ T = 443 \text{ K} \]
\[ k = 0.2972 \text{ min}^{-1}, \ T = 473 \text{ K} \]
Figure E4. Arrhenius plot of rate constant versus temperature for CO hydrogenation over Ru/SiO$_2$.
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