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Interactions of hydrogen with alkali promoted Ru/SiO$_2$ catalysts: A proton NMR study

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Interactions of hydrogen with alkali promoted

Ru/SiO$_2$ catalysts: A proton NMR study

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GENERAL INTRODUCTION

Currently, petroleum based fuel products holds the largest share in the energy resources. In addition, 95% of the world's chemical production is based on petroleum and natural gas. On the other hand, the oil reserves are limited and are expected to run out by the end of the next century (1). Since the natural gas reserves are expected to be exhausted at about the same time as those of crude oil, coal remains to be the only source of carbon which will be sufficient for several hundred years with the current demand of the petrochemical industry.

The synthesis of hydrocarbons from coal (Fischer Tropsch synthesis) is known since late 20s (2, 3). The process requires the gasification of coal with air and steam to produce what is known as syngas, a mixture of CO and H_2, and reacting this mixture on group VIII metals to produce hydrocarbons and oxygenates. In its most classical description, the Fischer Tropsch synthesis is a polymerization reaction which produces various oligomers regularly distributed along the carbon number range (5). The chemistry of methanation and FT synthesis process can be described by the following set of reactions (4):

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2O \tag{1}$$

$$CO + 2 H_2 \rightleftharpoons -CH_2- + H_2O \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

$$2\ CO \rightarrow C + CO_2 \hspace{4cm} (4)$$

Reactions 1-4 take place on every FT catalyst, but the selectivity of each catalyst determines the average product chain length (reaction 2), extent of coke deposition (reaction 4), and the extent of water-gas shift reaction (reaction 3). For example, Ni is a very active catalyst for reaction 1, but Co, Ru and Fe are selective for reaction 2. Therefore, the reaction of syngas over Ni catalyst produces mainly methane whereas a distribution of the hydrocarbon chain lengths is produced on Co, Ru or Fe catalysts. The selectivity of the catalyst towards reaction 3 determines whether the removal of oxygen consumes hydrogen or carbon monoxide, and hence shifts the equilibrium of reaction 2 towards right or left, respectively. The catalysts can also be modified by use of oxide supports and basic oxide promoters to alter the selectivity. For example, the selectivity of Co and Ru towards reaction 3 catalysts can be modified with the addition of potassium oxide: In the absence of potassium oxide, these catalysts mainly yield H_2O, whereas, potassium promoted Co catalysts give predominantly CO_2 (6).

Since reaction 2 is a polymerization reaction, the extent of The FT kinetics is mathematically describable by the Anderson-Schultz-Flory (ASF) distribution:

$$\ln\left(\frac{C_n}{n}\right) = n\ \ln\alpha + \ln\left[\frac{(1-\alpha)^2}{\alpha}\right] \hspace{3cm} (5)$$

where C_n is the mass fraction of the product hydrocarbons with n carbon atoms and α is the chain growth probability factor which can have values between 0 and 1 and is a direct measure of the selectivity of the catalyst towards reaction 2.

The chain growth probability factor, α, depends on the reaction conditions, the nature of the oxide support, the presence of basic promoters such as alkali metal oxides as well as the catalyst. For example, α increases with decreasing values of the H_2/CO ratio, decreasing reaction temperature and increasing pressure. Values of α are higher in the presence of alkali metal oxide promoters. Among FT active metals, α decreases in the order Ru>Co>Fe. Furthermore, catalysts supported on TiO_2 have higher α values than those supported on Al_2O_3 or SiO_2.

Despite the numerous efforts toward catalyst development and reactor design, present FT technology still suffers from the following limitations (4):

1.   Limited selectivity for premium products (e.g. light olefins, gasoline or diesel fuel);

2.   Catalyst deactivation;

3.   High capital cost;

4.   Heat removal;

5.   Less than optimum thermal efficiency.

The work presented in this dissertation is aimed at addressing the problems listed in items 1 and 2 by characterizing alkali promoted Ru/SiO_2 catalysts to bring about a better understanding of the role of the alkali promoters as the modifiers of

the metals and the supports. The engineering problems (items 3-5) are outside the scope of this work, but are listed for the sake of completeness. The remainder of this section is dedicated to providing the reader with a fundamental understanding of the work completed for this dissertation. Subsequent divisions state the objectives of the thesis research and summarize the work completed.

Explanation of the Dissertation Format

The research completed for this dissertation was written as six papers in a form suitable for publication in technical journals. Preceding the papers, a literature review and the research objectives are given. The general conclusions and recommendations for future work follows the papers. References cited in the general introduction and the literature review are listed following the recommendations for future work. The research reported in the six papers represents original work conducted by the author.

LITERATURE REVIEW

This section will be devoted to a general review of the Fischer Tropsch synthesis reaction. First the interactions of CO and hydrogen with metal surfaces will be reviewed. Then the CO hydrogenation reaction mechanisms will be covered based on the evidence from single crystal studies and the supported metal systems. Finally the role of promoters and oxide supports on the activity and the selectivity of the reaction will be discussed.

Fischer Tropsch Synthesis

To understand the role of the modifiers on the activity and selectivity of the FT synthesis products, a knowledge of the FT reaction mechanism is imperative. Due to the complexity of the reaction, research to date has not been able to provide a single FT mechanism. A few of the many unanswered questions that challenge present FT research are:

1. Whether CO bond scission occurs before CH bond formation;

2. The role of the secondary reactions;

3. The role of the oxide supports and catalyst modifiers such as alkali metal oxide promoters;

4. The structure sensitivity of the reaction.

In the following section, the literature to date will be reviewed selectively to give the reader an understanding of the existing theories and the experimental evidence about the interaction of CO with the supported metal catalysts and single

crystal surfaces. Subsequent sections will be devoted to the Fischer Tropsch

reaction mechanisms and the proposed roles of the modifiers, respectively.

CO Adsorption

The affinity of CO toward adsorption on metals determines the path and the

reaction products. For example, on Fe, Co, Ni and Ru, CO dissociation takes

place first and this type of catalyst has high activity in hydrocarbon formation; on

Pd and Rh, CO adsorbs molecularly and therefore these metals are selective

toward oxygenates. The heats of adsorption of CO and dihydrogen on Ni are very

close which explains why Ni is selective towards methane (7). Therefore,

understanding the interaction of CO and hydrogen with metal surfaces is crucial to

choose or design a catalyst selective for a specific FT synthesis product.

The adsorption of CO on metal surfaces takes place via a donation of

electrons from the metal surface to the bonding 5σ orbital and a back-donation

from $2\pi^*$ orbitals (31). Recent reports by extended Hückel calculations show that

the coordination of CO to group VIII transition metal surfaces depends on a subtle

balance of the interaction with the CO 5σ orbital, that tends to direct the CO

molecule to the atop position, and the CO $2\pi^*$ orbital, that directs the molecule to

the higher coordination sites. In the atop position, the changes in bonding to

different surfaces of the same metal can be mainly attributed to differences in the

interaction with the CO 5σ molecular orbital. The favored dissociation path is such

that carbon and oxygen atoms end up in high coordination sites, sharing as few

surface atoms as possible (32). The energetics involved in converting from the associative to the dissociative state involves both the heats of adsorption of the molecularly adsorbed states and the sum of the binding energies for adsorbed C and O atoms. For example, heats of adsorption of CO on Ru and Ni are comparable, but the sum of the binding energies of C_a and O_a are not. For that reason, the dissociation of associatively adsorbed CO is exothermic on Ni and endothermic on Ru (6).

Molecular adsorption of CO on metal surfaces results in mainly 4 different species (33-35, 41-42):

```
     O          O          O O          OOO
     |          |          | |          |||
     C          C          C C          CCC
     |          ^          V            V
     M          M M        M            M
   linear    bridging   di-carbonyl   multi-carbonyl
```
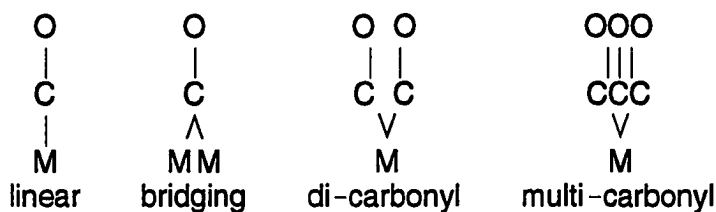
These different CO species on the metal surfaces are attributed to the local structure of the catalyst such as the edge and corner sites as well as the oxidative state of the particles themselves. For example, the multicarbonyl groups are believed to form on electron deficient metal atoms that are in close proximity with the support surface (35).

Since the initial bonding of CO on the surfaces is via the carbon atom, the dissociation proceeds via the vibrational deformation of M-C-O bond angle[1] which occurs more readily for multiply bonded than linearly bonded CO (6). In the presence of a promoter, CO may assume an IR inactive position such as tilted down or horizontal or even dissociated CO. This state is capable of reacting with hydrogen, but can not recombine and desorb as CO. Evidence for acetates and formates formed in the presence of the promoters is reported in literature, however; the reactivity of these species is not well established (30, 45).

The dissociative adsorption of CO on the metals should take place through at least two adjacent sites. Ponec (30 and references therein) reported evidence supporting an ensemble requirement for CO dissociation on Ni and Ru after studies on corresponding Cu alloys of these metals. Studies on supported Ni, Co and Ru catalysts as well as the single crystal surfaces of these metals yielded contradictory results on the structure sensitivity of the Fischer Tropsch synthesis reaction (36-40). For example, Geerlings *et al.* (39-40) reported that longer chain hydrocarbon fragments are formed on a zig zag grooved Co(11$\underline{2}$0) surface whereas on stepped Co(10$\underline{1}$2) and close packed Co(0001) surfaces mainly $CH_{x=1-3}$ species are observed. In addition, the Schultz-Flory distribution of the products yields different chain growth probabilities on the different surfaces. The chain growth probability for the Co(0001), (11$\underline{2}$0) and (10$\underline{1}$2) surfaces are reported as

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[1] A decrease in the vibrational frequency of the CO bond indicates an increase in the CO bond length. A decrease in CO vibrational frequency also means a decrease in the CO bond order (6).

0.2, 0.36 and 0.3, respectively. However, studies involving supported metal catalysts suggest that the differences that may appear as the effects of the metal particle size (i.e., structure sensitivity) may be due to the changes in the chemical nature of the support (4, 8, 37).

Proposed Fischer Tropsch Synthesis Mechanisms

Fischer and Tropsch (2, 3) suggested that CO reacts with the metal of the catalyst to form a bulk carbide which subsequently undergoes hydrogenation to form methylene groups. These species then polymerizes to form hydrocarbon chains, which later desorbed as saturated and unsaturated hydrocarbons. From this hypothesis, a number of chain growth schemes were proposed. Among these the most important are (5):

1. The $-CH_2-$ insertion scheme;

2. The CO insertion scheme;

3. The enolic mechanism;

4. The alkoxy mechanism.

These four mechanisms can be grouped into two broad categories (6, 57 and the references therein):

1. Carbide theory: The dissociative adsorption of CO on metal surfaces yield surface carbides which lead to formation of macromolecules. Hydrocracking of these macromolecules leads to the formation of low molecular weight olefins.

2. Enol theory: Molecularly adsorbed CO hydrogenates to form hydroxycarbene or enol, M=CH(OH), which can undergo further hydrogenation to form a methylene group. Different intermediates were suggested for an enol mechanism such as i) chain growth took place by condensation of enol groups with concurrent elimination of water; ii) CO insertion into the metal carbon bond of an adsorbed alkyl species and the hydrogenation of resulting acyl group produced water and a new alkyi group containing an additional methylene unit; iii) the chain is initiated by methyl groups formed by the stepwise hydrogenation of adsorbed hydrogen of molecularly adsorbed CO; iv) methyl groups might be formed by hydrogenation of surface carbon atoms, created by the dissociation of CO.

Although most recent developments support nonoxygenated intermediates as the precursors for the hydrocarbon chains, Henrici-Olivé and Olivé published a series of articles (8-10) suggesting that the CO insertion mechanism did not contradict with the data which suggested a carbidic mechanism or -CH_2-polymerization. Bell (6) and Kellner and Bell (11), on the other hand, favored the -CH_2- polymerization mechanism for the FT synthesis over Ru/Al_2O_3. Although current spectroscopic evidence is in favor of the -CH_2- insertion scheme for the clean surfaces, in the presence of promoters the possibility of having oxide intermediates have not, yet, been ruled out (45).

Residence time studies indicate that α-olefins are the primary products of the FT synthesis reaction which suggests that chain termination takes place via a β-hydrogen abstraction (9). With increasing residence times, α-olefin/paraffin ratio

decreases. Based on the previous reports on the residence time studies, Iglesia *et al.* (46-49) published a series of papers providing evidence for transport enhanced α-olefin readsorption which leads to an increase in the chain growth probability, α, and in paraffin content. Komaya and Bell (50) investigated the role of olefin reentry in the FT reaction on Ru/TiO_2. Their transient response experiments, coupled with a reaction model, strongly supported the reentry of ethylene in the chain growth process. However, they did not find any evidence for reentry of C_3+ olefins. Similarly, Pruski *et al.* (51) observed via NMR spectroscopy that ethylene adsorbed on Ru/SiO_2 reacted at room temperature to yield methane and n-butane in addition to strongly bound hydrocarbons.

Intermediates

The dissociative chemisorption of CO usually takes place via the Boudoard disproportionation reaction where CO_2 is released along with carbon deposition on the metal surface. Isolated carbon atoms deposited at temperatures below 300°C resemble carbidic carbons which irreversibly convert to the graphitic carbons upon heating. Similarly, graphitic carbon forms when CO adsorbs on the surfaces at high temperatures (6).

Duncan *et al.* (33) identified four forms of nonoxygenated carbon on the substrate after CO hydrogenation on SiO_2 supported and unsupported Ru, designated as C_α, $C_{\beta 1}$, $C_{\beta 2}$ and unreactive carbon. C_α was interpreted as carbidic carbon atoms distributed on or below the metal surface, $C_{\beta 1}$ and $C_{\beta 2}$ were alkyi

groups attached to the catalyst and they were differentiated by their relative mobilities and interconversion to other forms. The unreactive carbon had an NMR spectrum similar to turbostratic graphite. Later studies via isotopic tracer techniques on Ru/TiO_2 suggested that carbidic carbon, C_α, and alkyl carbon chains, C_β accumulated as reaction proceeded (52). It was also reported that the two different C_β pools served as precursors for different length hydrocarbon chain lengths: $C_{\beta 1}$ was the precursor of C_{2+} hydrocarbon products, while $C_{\beta 2}$ consisted of longer alkyl chains and did not participate in the production of gas phase products.

Temperature programmed desorption studies provided evidence for support stabilized methoxy (CH_3O) intermediates for methanation on Ni, Pt and Pd supported on Al_2O_3 (53 and references therein). The methoxy on alumina support hydrogenated at a faster rate than CO on Pt and Pd. But on Ni/Al_2O_3, CO hydrogenation rate was faster. By using atom superposition and electron delocalization molecular orbital (ASED-MO) theory, Anderson and Jen demonstrated that methoxy species move as an anion, OCH_3^-, from one Al^{3+} site to another, paired with a proton which moves from one O^{2-} to another (54). The reaction of this pair to form CH_4 was calculated to be energetically more favorable than the formation of CH_3OH. In the presence of alkali promoters, formate species may form during CO hydrogenation (55) or may be stabilized on the metal surface (45). In the light of these results, it seems impossible to modify the existing carbidic models (6, 51) to incorporate the effects of promoters.

The Role of Alkali Promoters

As indicated earlier, the FT reaction products have a distribution of the chain lengths described by the Anderson-Schultz-Flory distribution (Eq. 5). The selectivity of the reaction towards higher hydrocarbons can be enhanced by use of promoters such as alkali oxides or carbonates. Alkali promoters are not unique in their promotional effects but they are the cheapest and the most frequently used (29). Although their chemical state, physical location and mechanism by which they alter the reaction are not generally known, alkali metals have been reported to cause promotional effects including an increase in chain growth probability and a decrease in the rate of Fischer Tropsch synthesis over both Ru (14) and iron catalysts (15). So far, the following mechanisms have been postulated for these and other promotional effects induced by alkali metals:

1. Active metal site blocking for chemisorption (9, 16-18);

2. Electron donation to or from the metal (18-20);

3. Direct chemical interactions between adsorbate and the promoter (9, 12, 21, 22, 27);

4. Through space interactions (e.g., electrostatic) (23-25); and

5. Alkali induced surface reconstructions (26, 28).

In addition, alkali promoters can chemically interact with the oxide supports to change its acidity (43) or form chemically distinct, highly mobile species (44). The promoters can also stabilize the ionic forms of the active metals, M^+, and protect these against reduction (Madelung stabilization) which are the active

centers for oxygenate formation (30). One should remember that none of the above mechanisms are uniquely operable under reaction conditions. A more realistic picture involves several of these mechanisms taking place together.

Among all these mechanisms, Ponec (29-30) consistently rejected the electron donation from the alkali promoter to the metal catalyst as a mechanism for promotion for the following reasons:

i)   The alkali promoters are not in their electropositive metallic forms under reaction conditions.

ii) Solid state theory argues against massive transfer of electrons between a semiconductor (promoter or the support) and a metal. The theory predicts that the transfer of electrons form a semiconductor to the metal is limited to 2-3 electrons per hundred atoms at the metal semiconductor interface.

iii) Also, the field of a charge can not penetrate deep in the metal particle. At distances near the metal lattice constants, the external charges will be screened.

The studies on the role of alkali promoters have been conducted extensively on the single crystal surfaces (13, 20, 23, 27 and the references therein). However, the metallic form of the alkali promoters used in these systems makes the comparison with the supported catalysts systems difficult. In addition, the presence supporting oxide may have substantial effects on the selectivity of the FT reaction. For example, recent studies on the alumina supported and single crystal Co catalysts indicate that the chemical nature of the support surface may be the

controlling factor in determining the specific activity of supported cobalt catalysts (37). It was also reported that the presence of metal and/or promoters could influence the acidity of the supporting oxide significantly (43).

The Role of the Oxide Supports

The role of the supporting oxide material as an active participant in the FT synthesis has long been overlooked. The oxide supports may provide acidic or basic sites for chain initiation or dissociation. The support sites may also stabilize the reaction intermediates, therefore alter the reaction path (53-54). For example, transport enhanced olefin readsorption mechanism postulated by Iglesia and coworkers (46-49) involves the diffusion of the α-olefins on the support surface until readsorption to participate in chain growth. The nature of the support at the molecular level can easily alter the transport properties of the α-olefins and therefore the chain growth probability of the FT reaction.

The support material was shown to stabilize intermediates such as CH_3O for further hydrogenation to form methane (53). Therefore, although the individual reactivity of the support may not be significant, in the presence of spilled over intermediates, the support may serve more than just a structural promoter. Johnson et al. (37), for example, reported that the CO hydrogenation on Co was not a structure sensitive reaction and the differences in the activity and selectivity with different metal loadings had to be due to the differences in the chemical nature of the support. Similarly Jackson et al. (56) studied the adsorption of

hydrocarbons on Pt supported on different oxide materials. They attributed the differences in the hydrocarbon adsorption characteristics to the support oxide. In addition, they reported evidence for the interaction between the retained hydrocarbons and the OH groups of the silica support. Furthermore, the acidity and basicity of the support oxide can be influenced in the presence of metal ions. Fenyvesi *et al.* showed that alumina, silica and magnesia modified with metal ions such as Zr^{4+}, Li^+, Ca^{2+}, Nd^{3+}, and Ni^{2+} showed significant differences in the number and strength of the total acidity and/or basicity of these oxides (43).

RESEARCH OBJECTIVES

The general objective of this work completed for this dissertation was to elucidate the interactions between the alkali promoters and the hydrogen in the silica supported ruthenium catalysts. Alkali promoters are reported to enhance the selectivity of Fischer Tropsch synthesis reaction towards higher hydrocarbons on supported Ru, Fe and Co catalysts. However, the mechanism by which they modify the catalyst or how they alter the course of the reaction is not clearly understood. A significant number of studies done by vapor deposition of zerovalent alkali promoters on the single crystal surfaces of Ru suggested an interaction involving a transfer of electrons from the alkali metal to the substrate. Nevertheless, the results of these studies are not comparable with the supported metal catalyst systems for several reasons. First, the promoter is usually incorporated in the catalyst in the form of a salt which was eventually reduced or decomposed. The final form of the promoter is usually not zerovalent, and any zerovalent alkali metal formed during the reduction/decomposition stage leaves the catalyst surface due to their high vapor pressure in their metallic state. Second, the multifaceted metal surfaces involved in the supported catalysts complicates the interactions between the promoter and the catalyst. Finally, the promoter not only interacts with the catalyst, but also forms chemical compounds with the oxide supports.

The specific objectives of the research completed for this dissertation were:

1. To identify the chemical nature of the promoter after the thermal reduction in hydrogen.

2. To elucidate the nature of interaction between the promoter and the metal.

3. To characterize the silica support and monitor the changes in presence of the metal and the promoter.

To achieve these objectives, the following approach was implemented. The promoters were incorporated in the silica support via a co-impregnation and a sequential impregnation technique. Metal and/or promoter impregnation was carried out by an incipient wetness method. The reduction temperature of the catalyst and the final oxidative state of the promoter was determined by thermogravimetric analysis. The characterization of the silica support was carried out via proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The same technique was used to characterize the ruthenium surface by monitoring the interactions of the chemisorbed hydrogen on the metal. Quantitative nature of NMR spectroscopy enabled the author to monitor the site blocking nature of the alkali promoters. The electronic environment of the hydrogen was monitored via the changes in the Knight shifts in the hydrogen-on-metal resonances. Dynamic NMR studies were also conducted to elucidate the effect of the alkali promoters on the mobility of the chemisorbed hydrogen.

During the ^{1}H NMR characterization of the supported ruthenium catalysts, a strongly bound state of spilled over hydrogen was also identified. The effect of the

spilled over hydrogen on the hydrogen adsorption kinetics was elucidated and

quantity of the strongly bound spilled over hydrogen as a function of temperature

and hydrogen pressure was determined. A modified volumetric hydrogen

chemisorption technique was developed to minimize the interferences from the

strongly bound spilled over hydrogen.

REVIEW OF PAPERS WRITTEN

The work completed for this dissertation has resulted in the preparation of six papers for publication. The remainder of this section outlines the contents of the papers.

In paper 1, the role of potassium as a promoter of Ru/SiO_2 catalysts was investigated. The catalyst preparation technique determined the efficiency of the alkali incorporation on the metal surface. Potassium blocked more Ru sites for hydrogen chemisorption in the sequentially impregnated catalysts. In co-impregnated catalysts, NMR evidence suggested a decrease in the metal particle size with increasing alkali loading. The NMR lineshift did not change significantly which indicated the absence of electronic interactions between the promoter and the metal.

In paper 2, the results of Cs promoted catalyst characterization via proton NMR spectroscopy was reported. Upon hydrogen chemisorption, Cs promoter exhibited a unique behavior among the alkali promoters investigated (Na, K and Cs): even at the highest loadings of Cs, exposure of hydrogen caused elimination of Cs from the hydrogen chemisorption sites; The metal dispersions measured by strong hydrogen chemisorption were identical within the error limits of experimentation for all the Cs loadings. This effect was reversible upon thermal desorption of hydrogen. The interaction of Cs with the OH groups in the support created a resonance 10 ppm downfield of TMS. In the presence of spilled over

hydrogen, the intensities of both 3 ppm and 10 ppm resonances increased. Effect of Cs on the hydrogen mobility was also reported.

The effect of Na promoters on the chemlsorbed hydrogen was reported in paper 3. The conclusions of this work was similar to that of the K promoted catalysts. The dynamic NMR studies indicated that the presence of Na promoter significantly restricted hydrogen mobility on the metal surface. The absence of a weakly bound β state hydrogen suggested that Na preferentially occupied the edge and corner sites.

In paper 4, the interactions between the metal and/or the promoters and the silica support was reported. Three different proton populations were identified in the pure silica reduced and evacuated after being treated with distilled water via an incipient wetness technique. The overall proton density in the silica support decreased with the ruthenium metal loading, the alkali promoter loading and the catalyst reduction temperature. The affinity of the alkali promoters towards the exchange with the support hydroxyl groups decreased with the increasing atomic size (Na>K>Cs).

In paper 5, the role of spilled hydrogen on the catalyst characterization via volumetric hydrogen chemisorption was investigated. A strongly bound component of the spilled over hydrogen was identified. The effect of the weakly and strongly bound spilled over hydrogen on the kinetics of the hydrogen chemisorption was monitored via volumetric techniques and *in-situ* proton NMR spectroscopy. The hydrogen chemisorption on metal was completed within 10 min. as observed via

in-situ [1]NMR spectroscopy. However, hydrogen spillover took place over a time scale of 20+ hours. The ratio of the spilled over hydrogen to the hydrogen adsorbed on the metal decreased with increasing temperatures. The volumetric hydrogen chemisorption technique used in characterization of supported metal catalysts was modified to minimize the amount of the strongly bound spilled over hydrogen.

In paper 6, the nature of the spilled over hydrogen was discussed based on the proton NMR spectroscopic evidence. The absence of a change in the Knight shift of the hydrogen-on-metal resonance indicated that atomic hydrogen spilled over on the support. However, the spilled over hydrogen did not form O-H or Si-H bonds on the silica surface. Both reversibly and the irreversibly bound spilled over hydrogen possessed a high mobility as indicated by the decrease in the spin lattice relaxation times of the protons in the silanol groups.

**PAPER 1. HYDROGEN CHEMISORPTION ON POTASSIUM PROMOTED
SUPPORTED RUTHENIUM CATALYSTS**

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ABSTRACT

The interaction of hydrogen on potassium promoted catalysts prepared by both sequential and co-impregnation methods was studied by proton NMR spectroscopy. Potassium addition decreased the amounts of both hydrogen adsorbed on the metal (site blocking) and the support hydroxyl groups. No evidence for a ruthenium-mediated (through-metal) electronic interaction between potassium species and adsorbed hydrogen was found. During catalyst preparation, potassium was incorporated on the support by an exchange with the Si(OH) groups forming Si(OK) species, thereby reducing the amount of surface silanol protons. The sequential impregnation technique proved to be more efficient in depositing potassium on the metal surface.

INTRODUCTION

Alkali metals are often used as catalyst promoters for reactions such as ammonia synthesis (1, 2) and Fischer Tropsch synthesis (2). Although their chemical state, physical location and mechanism by which they alter the reaction are not generally known, alkali promoters have been reported to increase the chain growth probability and decrease the rate of Fischer Tropsch synthesis over both Ru (3) and iron catalysts (4). So far, several mechanisms have been postulated for these and other promotional effects induced by alkali metals: active metal site blocking for chemisorption (5-8); electron donation to or from the metal (7-10); direct chemical interactions between adsorbate and the promoter (7, 11, 12, 17); through space interactions (e.g., electrostatic) (13-15); and alkali induced surface reconstruction (16, 18).

It is generally accepted that for Fischer Tropsch catalysts such as rhodium (5, 8), ruthenium (3, 6) and iron (19), the presence of alkali promoters reduce the available surface sites for strong hydrogen and CO chemisorption. However, the existence of electronic interactions induced by the promoter is still not established. One major difficulty in understanding the promotional effects of alkali metals is that the chemical state(s) of the alkali species is not known. These states depend on the precursor used, catalyst pretreatment and the reaction (1). Strong electronic interactions of alkali with metals were suggested in extensive studies of single crystals (10, 20, 21 and the references therein). However, because zero valent

alkali was used in these studies, the comparison with real catalysts is difficult. Due to high vapor pressures (22) and relatively low heats of adsorption of zero valent alkali on ruthenium surfaces (20-70 kcal/mol) (41), it does not seem possible that they exist on the catalyst in the metallic state at reaction temperatures. Indeed, Aika et al. (1) noted that during the decomposition of $Cs(NO)_3$, any zero valent Cs species that formed evaporated immediately. Furthermore, compounds such as alkali carbonates are stable under the reaction conditions, reducing the possibility of electron donation to the metal substrate. Another fact one should observe is the extreme reactivity of alkali metals with all molecules containing protons (22). For example, upon adsorption of water on a full, dense layer of potassium on Ru(001), Thiel et al. (23) reported that water dissociated at 100 to 125 K to form adsorbed OH and H. It was shown that the reaction was not limited to the surface; instead, the dissociation products penetrated to the bulk and formed a three dimensional mixture of K and OH. Bonzel and Krebs (24) observed formation of KOH and K_2CO_3 on Fe surfaces upon exposure to CO/H_2 mixtures.

It has also been suggested that the ionic character of alkali promoters induces an electrostatic field which may result in a significant promotional effect, at least on single crystal surfaces (14). Studies of supported catalysts, however, showed that these electrostatic fields of alkali promoters did not strongly affect the catalyst surface-adsorbate interactions (8, 15). For example, Compton and Root (8) showed that the NMR lineshift of CO adsorbed on alkali promoted Rh/SiO_2 was too large to be due to solely an electrostatic effect. Oukaci et al. (15) studied the

effect of group 1A cations on CO hydrogenation over Ru/Y-Zeolites and tested the postulate that the exchange of sodium ions with smaller or larger cations produces a change in the electrostatic field inside the zeolite, and hence a change in their acid strengths. They found no evidence of electronic or electrostatic interactions influencing the specific activity of the catalysts or the overall chain growth probability.

Somorjai and Van Hove (18) recently reviewed the literature on adsorbate induced restructuring of surfaces and reported that vapor deposited alkali metals induced surface reconstructions of Ni, Cu, and Pd single crystal surfaces producing "missing row structures". Hayden *et al.* (16) observed a (1X2) reconstruction of a Ag(110) surface upon adsorption of small amounts of Li, K and Cs ($0.05 < \Theta < 0.2$) at 300 K. They suggested increased density of states at the Fermi level resulted in the reconstruction. Again these studies used zero valent alkali as adsorbates.

The method of alkali incorporation in the catalyst plays an important role in how alkali partitions itself between the metal and the support surfaces (5, 8). Kesraoui *et al.* (5) have noted that a co-impregnation technique influenced the metal particle size in supported rhodium catalysts. When potassium was co-impregnated with rhodium on silica at a Rh:K atomic ratio of 2:1, a significant increase in hydrogen uptake was observed relative to unpromoted catalysts. Also the crystallite size measured by X-ray diffraction decreased below the 4 nm detection limit from a value of 12.5 nm for the unpromoted catalyst. When

potassium promoted catalysts were prepared by a sequential impregnation technique, Compton and Root (8) observed differences in alkali incorporation on the support depending on how the Rh/SiO_2 substrate was prepared. For Rh/SiO_2 prepared by using amine exchange, they observed that NH_4^+ species existed on the support in the form of $SiONH_4$. This species prevented support protons from exchanging with potassium. In catalysts prepared by wet impregnation, however, potassium was able to replace some of the silanol protons.

Proton NMR has proven to be a useful tool to quantitatively and qualitatively characterize supported metal catalysts (25-30). Also, the Knight shift variation of the hydrogen-on-metal peak can be used to estimate the extent of induced electronic interactions affecting the chemisorbed hydrogen (26-31). The purpose of the work reported here was to determine the effect of potassium promotion on the nature of the chemisorbed hydrogen in silica supported ruthenium catalysts. In addition, the partitioning of the alkali promoter between the metal and the support was investigated.

METHODS

Catalyst Preparation

All catalysts in this study were prepared via incipient wetness. Ruthenium nitrosyl nitrate, $Ru(NO)(NO)_3$ solution (1.5 wt% ruthenium, Strem Chemicals), ruthenium nitrosyl nitrate (26 wt% Ru, Johnson Matthey) and potassium nitrate (Johnson Matthey) were used as precursors. Potassium was incorporated into the catalysts by both sequential impregnation and co-impregnation. In sequential impregnation, a sufficient amount of ruthenium nitrosyl nitrate (Johnson Matthey) was dissolved in 2.2 ml water/g of support to yield a metal loading of 4 wt% in the reduced catalyst. Then a slurry was prepared by mixing an appropriate amount of silica (Cab-O-Sil HS-5) in the ruthenium nitrosyl nitrate solution, dried overnight at room temperature and then for 4 h in air at 383 K. The unpromoted catalyst was reduced in flowing hydrogen for two hours at 623 K. The reduced catalyst had a Ru dispersion of about 10% measured by strong hydrogen chemisorption (33). After reduction, the 4% Ru/SiO_2 catalyst was impregnated with the potassium nitrate solution of the desired composition such that 2.2 ml solution per gram of support resulted in the appropriate potassium loading (2, 10, 15, 20 and 40 atomic percent of the total metal amount). The catalysts were dried in air at room temperature overnight and then at 383 K for two hours. Potassium loadings were confirmed by atomic absorption spectroscopy.

For catalysts prepared by co-impregnation, potassium nitrate was mixed with the ruthenium nitrosyl nitrate solution (Strem Chemicals). The ruthenium loading was kept at 4 wt% by using 2.6 ml solution (1.5 wt% Ru) per gram of support. The amount of potassium nitrate was adjusted to obtain potassium loadings of 33.3, 50, 66.6 and 75 atomic percent of the total metals. The same drying procedure as above was used. After reduction, the unpromoted catalyst had a dispersion of approximately 18% measured by strong hydrogen chemisorption (33).

Thermogravimetric Analysis (TGA) Experiments

Thermogravimetric measurements of 20 mg catalyst samples were conducted in a Perkin Elmer TGA 7 analyzer interfaced with a PE-7500 computer for data acquisition and automatic control of the experiment. Experiments were done under a gas flow of 40 cc/min. Mass flow controllers were used to adjust the flow rate of a 10% hydrogen, 90% helium mixture. Heating rates of 1 to 10 K/min were used depending on the temperature response of the sample under study.

NMR Sample Preparation

About 30 mg of catalyst was placed in 5 mm O.D. NMR tubes and then attached to sample ports of an adsorption apparatus described elsewhere (25). Subsequently, 760 torr of helium was introduced in to the cell and the sample was heated to 423 K for 30 min, evacuated and dosed with approximately 100 torr of

hydrogen. After the temperature was increased to 623 K at a rate of 6 K/min, samples were evacuated and 760 torr of fresh hydrogen was introduced. This evacuation/hydrogen replacement cycle at 623 K was repeated every 30 min. for 2 hours. After reduction, the samples were evacuated for 4 hours at the reduction temperature and then allowed to cool to room temperature. Each sample was then dosed with hydrogen at about 100 torr, equilibrated for 1 hour and evacuated to 10^{-5} torr for 5 minutes. Finally, the samples were immersed in a water bath, sealed with a microtorch and weighed. The net weight of the catalyst sample was obtained by deducting the weight of the empty tube from the final weight of the sealed sample.

NMR Experiments

A home built spectrometer with resonance frequency of 220 MHz was used for ^{1}H NMR experiments. All proton NMR spectra of hydrogen-dosed catalysts consisted of two peaks: one associated with the silanol protons from the support and the other representing the hydrogen on the metal particles (25). At a recycle time of 0.2 to 0.4 s the full recovery of the metal peak was established but the silanol peak intensity was suppressed due to its longer spin-lattice relaxation time. When the full intensity of the silanol peak was investigated, the recycle time was set at 70 seconds to restore the equilibrium magnetization. The spin lattice relaxation times, T1, of hydrogen on the metal were determined by the null point method (32).

Absolute intensities were obtained by referring to a water sample doped with trace amounts of $FeCl_3$. The reference sample was sealed in a capillary tube of the length of the catalyst samples to account for field inhomogeneities in the NMR coil (25). All NMR measurements were performed at 294 ± 1 K.

RESULTS

Thermogravimetric analyses were done on potassium nitrate and the catalysts to help identify the chemical state of the alkali species after the decomposition and reduction pretreatment steps. The effect of the reducing environment on the decomposition of catalyst precursors is shown in Fig. 1. The decomposition of potassium nitrate in flowing helium resulted in a smooth weight loss beginning at a temperature of about 850 K (Fig. 1.d). Switching to a flowing mixture of 10% hydrogen in helium resulted in a decomposition beginning significantly earlier (Fig. 1.c). At about 880 K, 57% of the initial total weight was lost. The residual weight was assigned to K_2O based on the relative fraction of K_2O in $(KNO_3)_2$ (42.6%). Further heating in the reducing atmosphere resulted in total loss of the material. A similar treatment on the unpromoted 4% Ru/SiO_2 indicated that reduction occurred around 445 K (Fig. 1a), whereas the promoted catalyst consisting of 4 wt% Ru on SiO_2 and a Ru:K ratio of 2:1 reduced at a temperature of 480 K (Fig. 1b). At higher levels of promotion the reduction temperature of the catalyst remained constant within the error limits of experimentation (± 2 K). The TGA of potassium promoted catalysts did not show any feature around 880 K where potassium nitrate decomposed. This indicated that the presence of ruthenium catalyzed the decomposition of potassium nitrate.
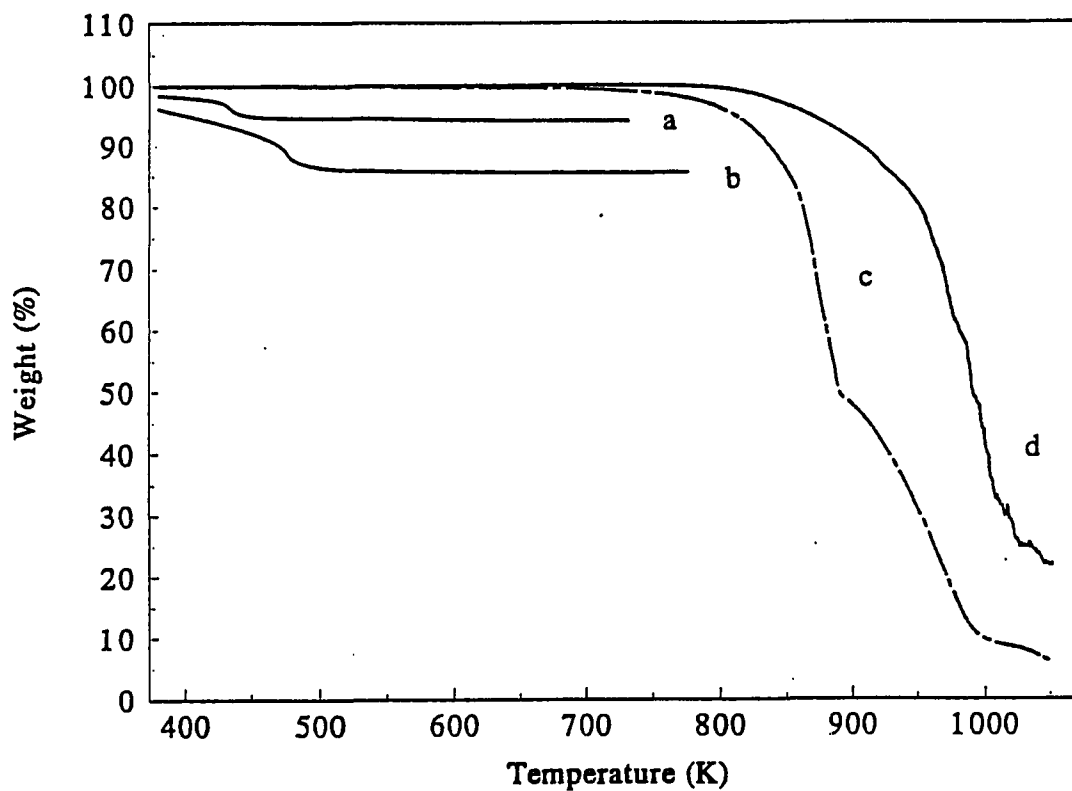
Figure 1. The results of the thermogravimetric analysis of (a) 4%Ru/SiO$_2$;
(b) 4%Ru/SiO$_2$ co-impregnated with potassium at a K:Ru atomic ratio of
2:1; (c) potassium nitrate in the presence and (d) in the absence of a
reducing atmosphere

The ^1H NMR spectra of strongly bound hydrogen in a series of sequentially-impregnated, potassium-promoted catalysts are shown in Fig. 2. The upfield peak (-60 ppm) in each spectrum was identified as hydrogen dissociatively chemisorbed on ruthenium and the downfield peak (3 ppm) was assigned to the silanol protons (25). The upfield peak was best fit by an exponential Gaussian function and for the peak at 3 ppm a superposition of one sharp Lorenzian and one broad Gaussian peak was used. The NMR spectra for the co-impregnated series of catalysts are shown in Fig. 3. In these spectra, a third peak appeared at approximately 20 ppm at potassium loadings of 50 atomic % and higher.

The results presented in Figs. 2 and 3 indicated that the NMR intensity of the hydrogen-on-metal peak decreased significantly with potassium loading. However, this change of intensity was not accompanied by a meaningful shift of the hydrogen-on-metal resonance (Fig. 4). We, thus, assume peak at ~-60 ppm represents hydrogen on Ru only which is not in the fast exchange limit with any other form of hydrogen in the catalyst. Consequently, meaningful quantitative information can be obtained from the intensities of the hydrogen-on-metal resonances. The strongly bound hydrogen coverage, Θ_H, can be now obtained by measuring the integrated intensity of the NMR resonance at ~-60 ppm. Also, the potassium coverages on ruthenium can be indirectly estimated from the strongly bound hydrogen coverages, $\Theta_K=1-\Theta_H$, (Figs. 4 and 7). A plot of NMR intensity of strongly bound hydrogen on Ru versus potassium-to-ruthenium molar ratio is
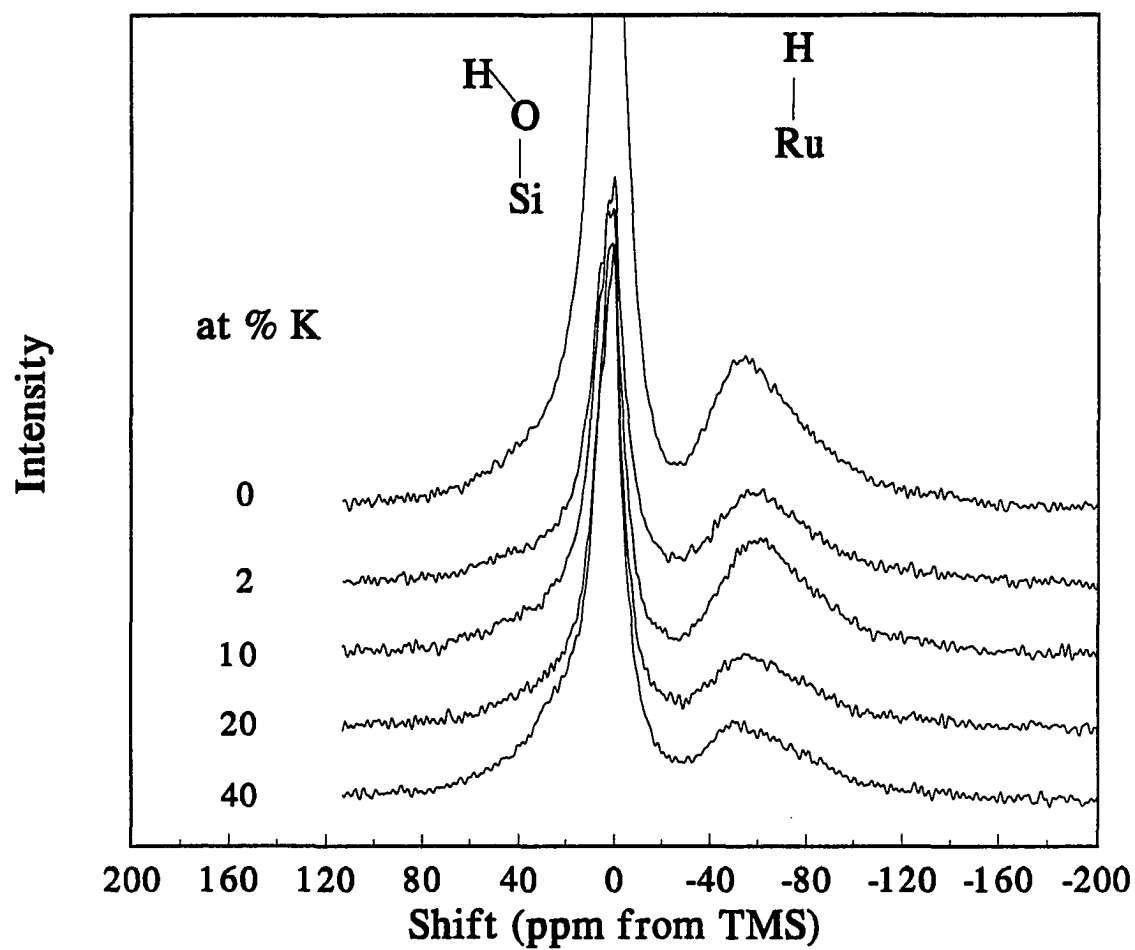
Figure 2. ^{1}H NMR spectra of sequentially impregnated K/Ru/SiO$_2$ catalysts. Each of the spectra shown is obtained by averaging 1000 scans
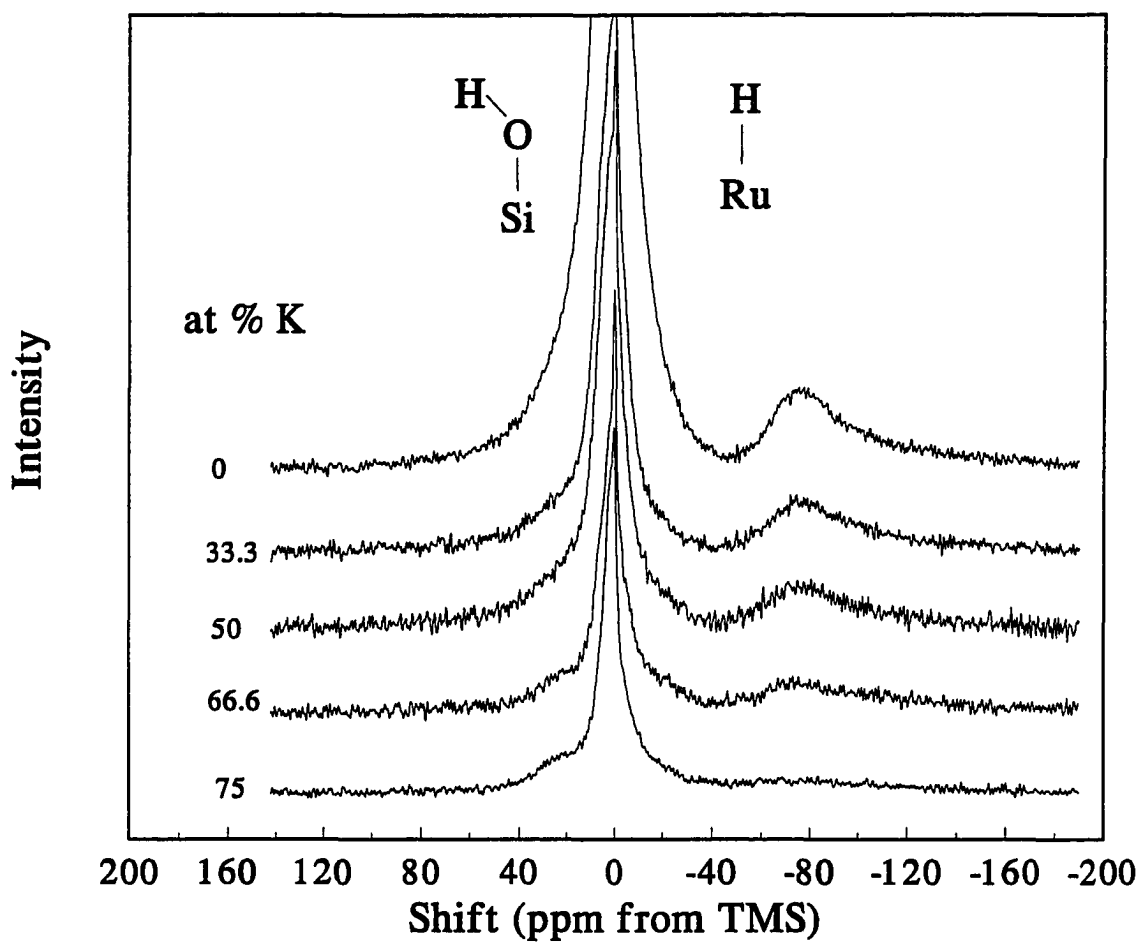
Figure 3. ¹H NMR spectra of co-impregnated K/Ru/SiO$_2$ catalysts. Each of the spectra shown is obtained by averaging 1000 scans
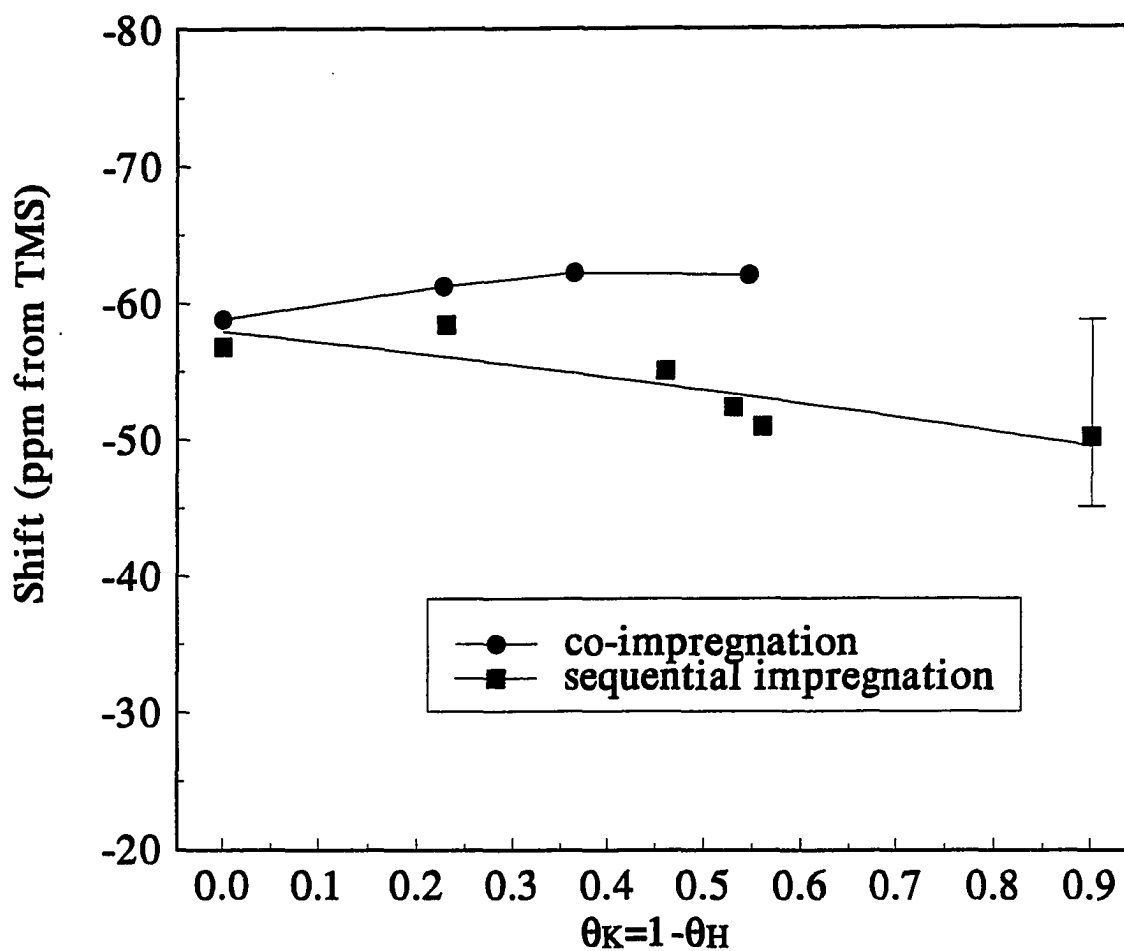
Figure 4. The change in hydrogen-on metal resonance as a function of potassium coverage (see text)

shown in Fig. 5. The dashed line on the plot indicates the amount of Ru sites blocked assuming that each potassium atom covers one metal atom site. The experimental curves follow a generally less negative slope indicating that the site blocking effect of potassium was not on a one-to-one basis. The co-impregnated catalysts exhibited a significantly smaller decrease in the number of hydrogen chemisorption sites compared to the sequentially impregnated catalysts. The loss of silanol proton intensities as a function of total potassium loading are plotted in Fig. 6. The results show that the silanol peak intensity diminished with increasing potassium loading. The co-impregnated catalyst series displayed a greater silanol intensity decrease upon potassium addition.

Spin lattice relaxation times were determined for the hydrogen-on-metal resonance. The spin lattice relaxation time, T1, of the strongly bound hydrogen is plotted in Fig. 7 as a function of surface hydrogen coverage. T1s of the chemisorbed hydrogen on ruthenium exhibited a small increase with potassium metal content for both the co-impregnated and sequentially impregnated series. These values are consistent with the spin-lattice relaxation times of protons interacting with conduction electrons.
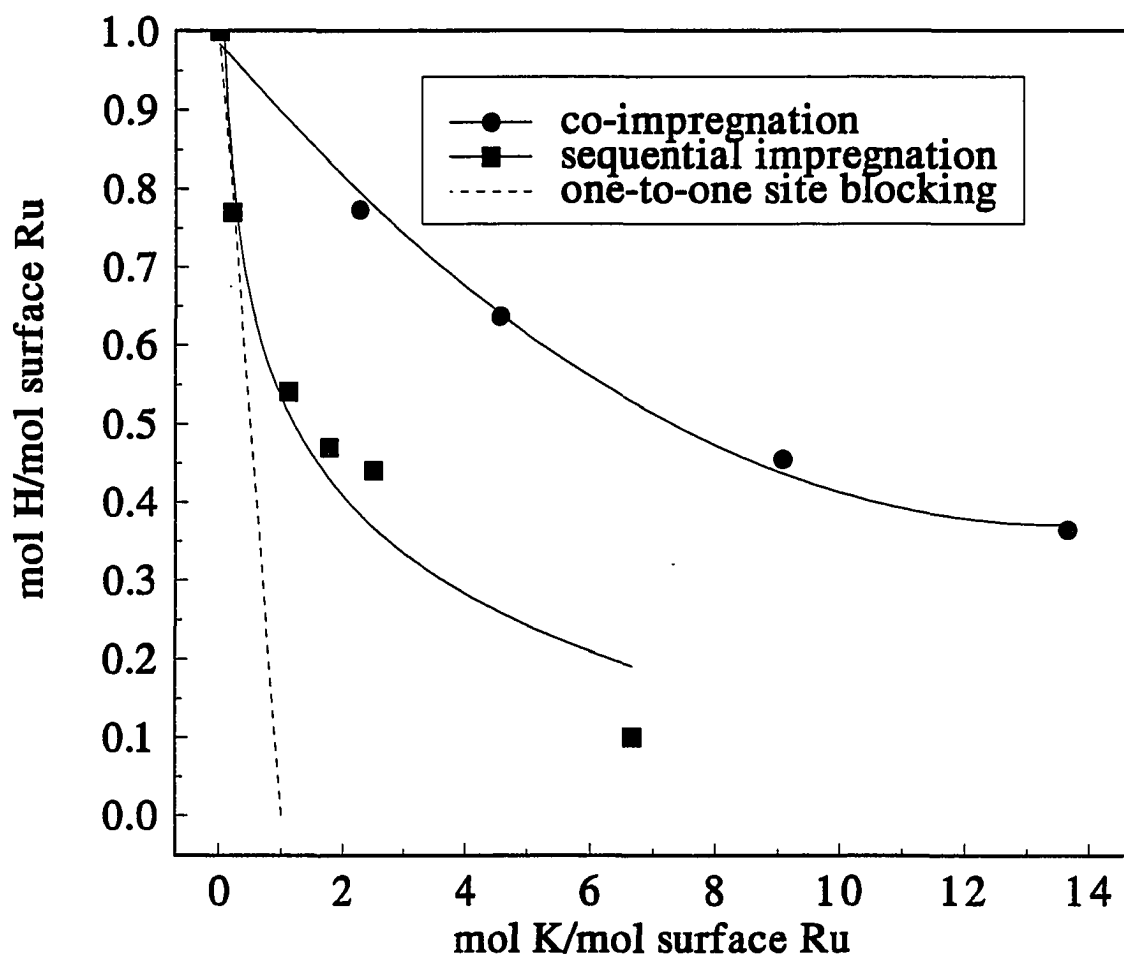
Figure 5. Change in NMR intensity of the hydrogen-on-metal resonance as a function of alkali loading. The dashed line represents the case where each alkali atom would have blocked one hydrogen chemisorption site on ruthenium particles
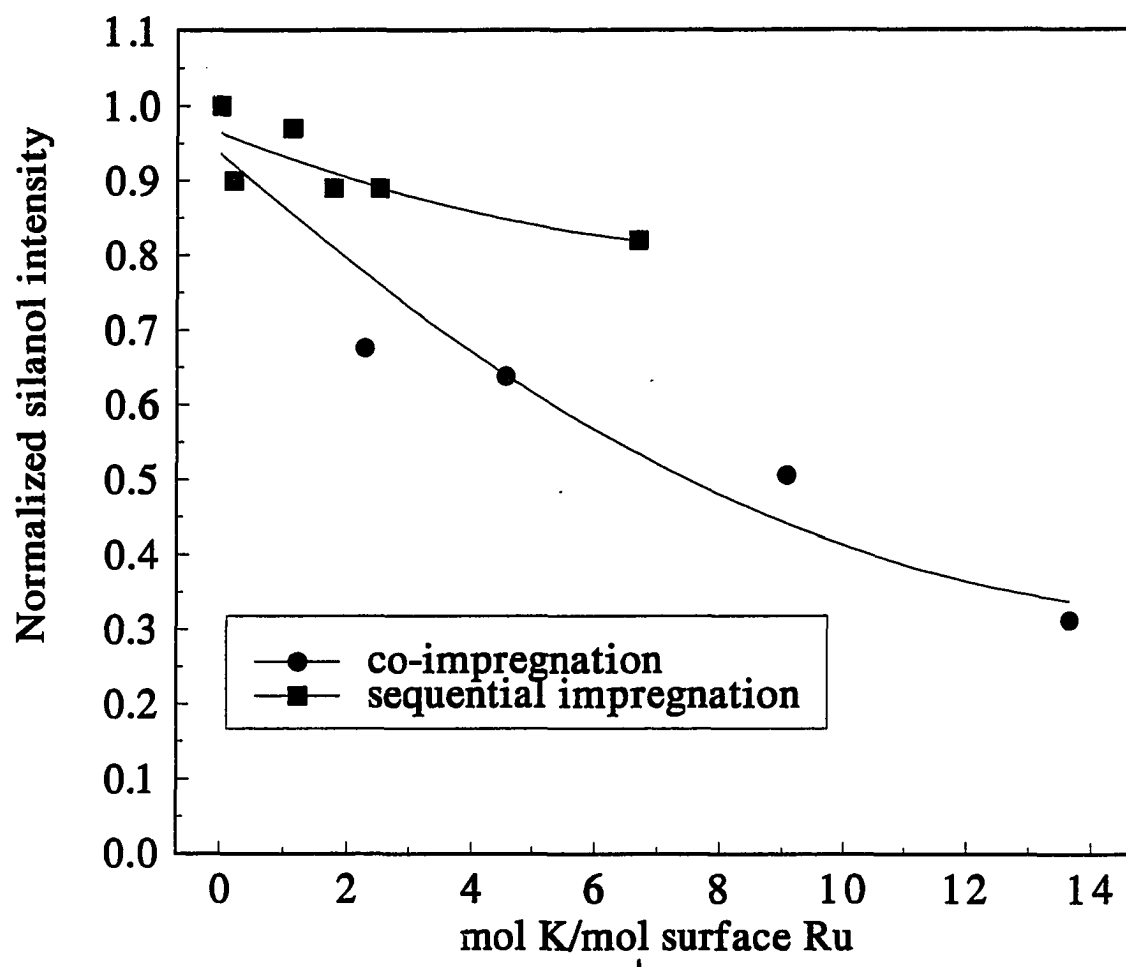
Figure 6. Change in relative silanol peak intensity as a function of potassium
loading. The silanol intensity was normalized with respect to the silanol
intensity of the unpromoted catalyst
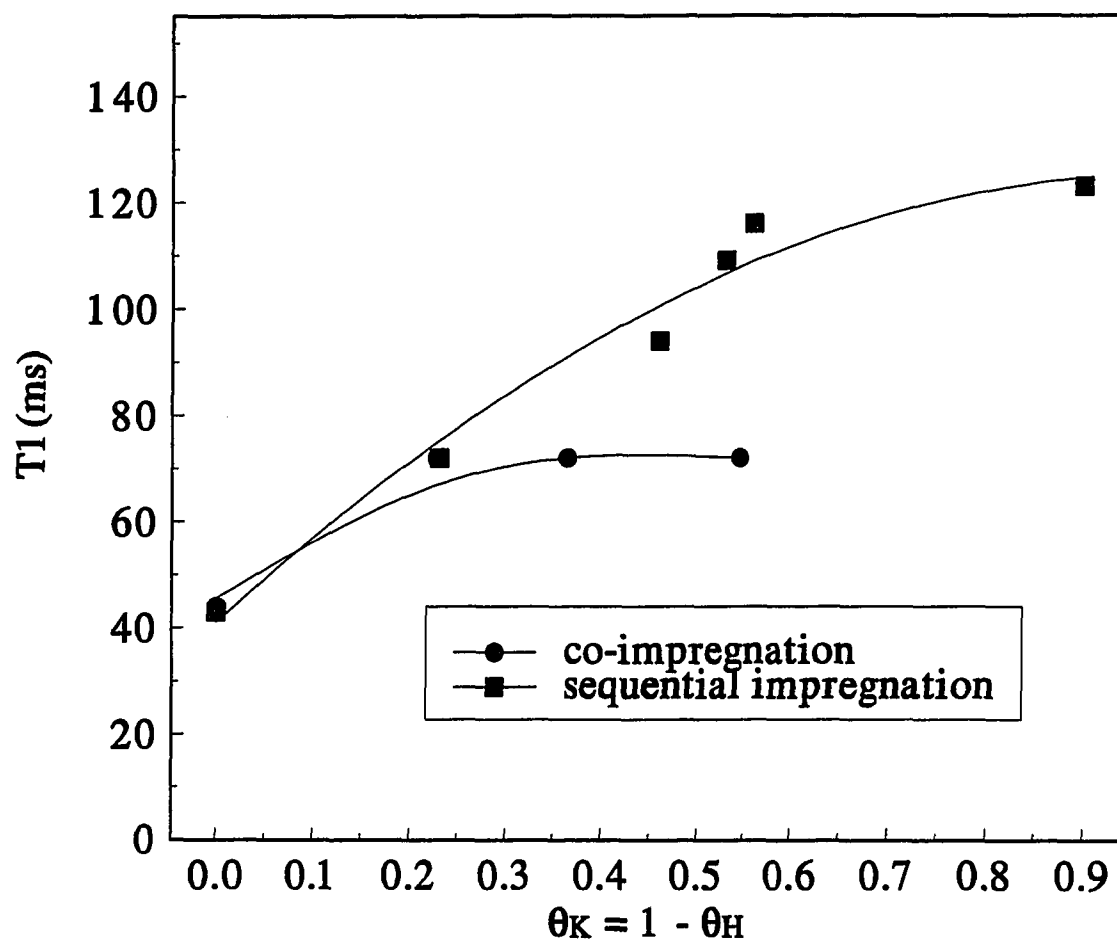
Figure 7. Spin lattice relaxation times of hydrogen on metal resonances as a function of surface hydrogen coverage

DISCUSSION

Catalyst Reducibility

The thermogravimetric analysis of unpromoted 4%Ru/SiO$_2$ (Fig. 1a) indicated that the reduction temperature of the precursor, Ru(NO)(NO$_3$)$_3$, (not shown) did not change appreciably in the presence of the silica support. The TGA results for KNO$_3$ indicated a 57% weight loss by about 880 K corresponding to the formation of K$_2$O. Further heating resulted in evaporation of this species. Although the presence of ruthenium metal may alter the nature of the decomposition products, TGA showed that the oxide form of potassium existed after the pretreatment of the catalyst. This agrees with the results of Aika et al. (1) who reported the formation of Cs$_2$O, Cs$_2$O$_2$ and CsOH species upon decomposition of CsNO$_3$ in the presence of Ru. Their results suggest that any Cs metal formed during the disproportionation of Cs$_2$O evaporated immediately. Similarly, De Paola et al. (34) reported that co-adsorption of potassium and oxygen on Ru(001) yielded stable KO$_2$ and K$_2$O$_2$ compounds. The thermogravimetric analysis of the co-impregnated catalysts indicated an increase in the reduction temperature of the potassium promoted catalyst by ~35 K relative to the unpromoted catalyst. A change in potassium loading did not cause noticeable changes in the reduction temperature of the catalysts. Similar increases in catalyst reduction temperatures have been observed for alkali promoted molybdate catalyst systems (35). It is also

noted here that both the metal and the promoter precursors reduced simultaneously suggesting a synergistic effect.

Potassium Partitioning between Metal and Support

The ^{1}H NMR measurements of surface coverage as a function of potassium loading strongly suggest that the adsorption sites are blocked but not on a one-to-one basis. Hoost and Goodwin (6) reported a one-to-one blocking of hydrogen adsorption sites with potassium loading on a Ru/SiO_2 catalyst. This discrepancy may be due to the different catalyst preparation methods and characterization techniques used in our work. For example, Hoost and Goodwin (6) used a higher reduction temperature of 673 K and characterized their catalysts via volumetric hydrogen chemisorption. We have noted with ^{1}H NMR spectroscopy a strongly bound, spilled over hydrogen on the silica support which is not distinguishable in the volumetric experiment (33). The amount of spilled over hydrogen depended on factors such as reduction temperature and presence of alkali promoters. In addition, the higher reduction temperature used in their work may have changed the potassium distribution on the metal particle surfaces. For example, Compton and Root (36) observed a change in CO adsorption states on potassium promoted Rh/SiO_2 surfaces upon reduction at elevated temperatures. According to their results, higher reduction temperatures helped redistribute the promoter on the metal surface: a low potassium loading catalyst reduced at high temperatures resembled a high potassium loading catalyst reduced at high temperatures.

To confirm that potassium partitioned itself between the metal and the support, quantitative intensity measurements of the silanol protons were conducted. The relative change in the silanol intensity as a function of potassium loading given in Fig. 6 was normalized to the value obtained for an unpromoted catalyst. The simultaneous decrease in the intensities of the silanol and the hydrogen-on-metal resonances as a function of potassium loading suggests that the potassium species blocked the hydrogen chemisorption sites on the metal surface and also eliminated the silanol protons from the surface of the support. In addition to the intensity decrease of the silanol protons with potassium loading, an additional resonance at around 20 ppm in catalysts with potassium loadings exceeding 50 at% confirmed that potassium partitioned itself onto the support (Fig. 3). It is noted that the appearance of the resonance at 20 ppm did not affect the lineshift of hydrogen chemisorbed on metal particles (-60 ppm) which suggested the lack of a fast exchange between the two species. The resonance at around 20 ppm was also observed in a sample consisting of potassium impregnated onto the silica support without ruthenium metal (not shown). This resonance was suggestive of KOH based on proton NMR experiments on pure KOH samples done in our lab. This assignment is consistent with the previously reported results of potassium hydroxide species on Fe and Ru single crystals (17, 23, 24). Furthermore, thermodynamics dictates that in the presence of even trace amounts of water, K_2O forms KOH at typical reduction temperatures (44). Therefore we

conclude that potassium is present in these catalysts as a mixture of oxide and hydroxide states.

The catalysts prepared via the co-impregnation technique exhibited a smaller change in hydrogen-on-metal resonance intensity and a larger change in support hydroxyl intensity compared to the catalysts prepared via the sequential impregnation. We attribute this effect to the decrease in the metal particle size with potassium loading upon co-impregnation. A similar effect has been observed previously for potassium promoted Rh catalysts (5). It is unlikely that the above effect results from K exchanging more readily with the support protons in the case of co-impregnated catalysts. The exchange efficiency of potassium with the OH groups of the support depends on pH. Since the isoelectronic point of silica is around a pH of 1 to 2, at pH values lower than 2 the surface of the support will be positively charged which will inhibit the cation exchange. Therefore, it is not expected that potassium would have a higher affinity for the support surface in the co-impregnation solution (pH<1) in comparison to the sequential impregnation technique where the potassium impregnation solution has a higher pH.

Electronic Interactions

A significant number of papers have reported that alkali metals adsorbed on Ru single crystal surfaces change the electronic structure of the substrate (10, 13, 14, 21, 37). For example, Hrbek (37) reported that the work function of a Ru(001) surface exhibited a minimum as a function of alkali coverage. Addition of

hydrogen did not influence the work function of an alkali precovered Ru(001) surface (38) which was consistent with the results determined for hydrogen on a clean surface (39).

These and similar studies have led researchers to postulate that a possible mechanism for alkali promotion in supported metal catalysts involves transfer of electron density from the alkali species to the metal particle. However, the results presented here argue against the suggestion of a through-metal electronic interaction. The hyperfine interactions of unpaired conduction electrons with the probe nucleus (in this case ^1H) can produce large shifts of NMR lines (Knight shift) (40). Hence, a change in the Knight shift indicates a change in the density of the bonding states at the Fermi level. The results presented in Fig. 4 indicated the maximum variation in the shift was ±10% even at potassium loadings such that 90% of the available ruthenium surface was blocked. This change is well within the range due to particle size variations for the co-impregnated catalysts (25) and experimental error. Since the observed Knight shift of the hydrogen-on-metal resonance did not change significantly, we conclude that strong electronic interactions were not operable. In contrast, a large change in the Knight shift of chemisorbed hydrogen was noted with Cl poisoning of a Ru/SiO_2 catalyst (27). This conclusion of the lack of a through-metal interaction is consistent with the observation that potassium is not present in the form of a zero valent species but rather as the oxide (noted by TGA), or the hydroxide. Alkali metals present in catalysts as oxides are unlikely to donate electron density to the metal particle.

For example, LEED analysis of co-adsorbed Cs and O atoms on a Ru(0001) surface indicated that the bond lengths were modified in a way consistent with an effective transfer of electronic charge from Cs to O (45). As indicated by Ponec and coworkers (42, 43), the transfer of electron density is not likely to occur to an appreciable extent such that the catalytic properties of the metal particle can be altered.

CONCLUSIONS

The effect of potassium promotion on hydrogen chemisorption on a series of Ru/SiO$_2$ catalysts was investigated by proton NMR spectroscopy. Potassium species were found both on the metal and on the support surfaces. Sequential impregnation was more efficient in incorporating potassium onto the metal surface. The co-impregnation technique resulted in a greater loss of hydroxyl protons on the support surface. The NMR results indicated no evidence of "through-ruthenium" electronic interactions between potassium and hydrogen, at least as noted by the ^{1}H NMR Knight shift which is sensitive to the density of the bonding states at the Fermi surface. However, potassium species blocked the metal sites available for hydrogen chemisorption. ^{1}H NMR spectroscopy indicated the formation of KOH on the support surface.

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ACKNOWLEDGEMENTS

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**PAPER 2. THE ROLE OF Cs PROMOTER IN FISCHER TROPSCH
SYHNTHESIS ON Ru/SiO$_2$ SURFACES**

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ABSTRACT

Cs promoted Ru/SiO$_2$ catalysts were characterized via ^{1}H NMR spectroscopy. Contrary to the results of studies using single crystals, we did not find any evidence of a ruthenium-mediated electronic interaction between the Cs promoter and adsorbed hydrogen at least as indicated by the proton Knight shifts. The site blocking effects of the Cs promoter diminished after exposure to hydrogen for extended periods of times. This effect was reversible after thermal evacuation of the hydrogen. In the presence of Cs, the surface of the support was also modified; the intensity of the diamagnetic resonance in the spectrum (predominantly Si-OH) decreased, and an additional resonance appeared in the spectra. The mobility of the hydrogen on the Ru surface and at the metal-support interface (spillover) was restricted in the presence of Cs. We postulate that this restricted mobility of hydrogen can account for the increased chain growth probability in the presence of alkali promoters.

INTRODUCTION

The synthesis of hydrocarbons from coal (Fischer Tropsch synthesis) has been known since late 1920s (1-2). The process requires gasifying coal with air and steam to produce syngas, a mixture of CO and H_2, and reacting this mixture on group VIII metals to produce hydrocarbons and oxygenates. In its most classical description, the Fischer Tropsch synthesis is a polymerization reaction that produces various oligomers regularly distributed along the carbon number range (3). The extent of the Fischer Tropsch synthesis reaction is mathematically describable by the Anderson-Schultz-Flory distribution (3). The selectivity of the catalyst toward higher hydrocarbons depends on the reaction conditions, the nature of the oxide support, the presence of basic promoters such as alkali metal oxides, and the catalyst. For example, the selectivity towards higher hydrocarbons increases with decreasing values of H_2/CO ratio, decreasing reaction temperature, and increasing pressure. Furthermore, catalysts supported on TiO_2 have higher selectivities towards higher hydrocarbons than those supported on Al_2O_3 or SiO_2 (4-5). The selectivity of the reaction toward higher hydrocarbons can be enhanced by use of promoters such as alkali oxides or carbonates. Alkali promoters are not unique in their promotional effects, but they are the cheapest and the most frequently used (6).

Research to date has suggested several mechanisms for the role of alkali promoters in the Fischer Tropsch synthesis. A more general review of these

mechanisms can be found elsewhere (7-8). In summary, the existing theories for alkali promotion include active metal site blocking for chemisorption, electron donation to or from the metal, direct chemical interactions between adsorbate and promoter, through-space interactions (e.g., electrostatic), and alkali-induced surface reconstruction. The promoters can also stabilize the ionic forms of the active metals, M^+, which are the active centers for oxygenate formation (9), and protect these against reduction (Madelung stabilization). In addition, alkali promoters can chemically interact with the oxide supports to change their acidity (10) or form chemically distinct, highly mobile species (11).

The mechanisms of alkali promotion postulated in the literature focus mainly on the role of alkali promoters in the modification of metal surfaces. It is also known that basic alkalis readily form chemical compounds with many of the commonly used supports, such as silica, alumina, or titania. Therefore, the presence of the promoters influences the overall acidity or the basicity of the supported catalysts (12). Although the individual effect of the support is not clearly understood, its role in the overall performance of the catalyst is recognized. For example, the transport-enhanced olefin readsorption mechanism postulated by Iglesia and coworkers involves the diffusion of α-olefins on the support surface. These olefins can then readsorb on metal particles where they participate in subsequent chain growth (13-16). In such cases, the nature of the support at the molecular level can easily alter the transport properties of the α-olefins and therefore the chain growth probability of the Fischer Tropsch synthesis reaction.

Furthermore, the support material was shown to stabilize intermediates such as CH_3O for further hydrogenation to form methane (17).

In addition to the alkali promotion mechanisms postulated above, we will investigate the effect of the alkali promoter on the adsorbate dynamics by using some unique capabilities of the NMR spectroscopy (18). The reason we selected hydrogen as an adsorbate are threefold: (i) ^1H NMR is relatively easy to perform, (ii) hydrogen is one of the reactants in the Fischer Tropsch synthesis and (iii) hydrogen is an excellent probe nucleus for investigating the surface structure and composition of the supported metal catalysts.

METHODS

Catalyst Preparation

All catalysts in this study were prepared via incipient wetness. First, a sufficient amount of ruthenium nitrosyl nitrate (Johnson Matthey) was dissolved in 2.2 ml water/g of support to yield a metal loading of 10 wt% in the reduced catalyst. Then a slurry was prepared by mixing an appropriate amount of silica (Cab-O-Sil HS-5) in the ruthenium nitrosyl nitrate solution and dried overnight at room temperature and then for 4 hours in air at 383 K. The unpromoted catalyst was reduced in flowing hydrogen for 2 hours at 623 K. Cesium was incorporated into the catalyst by sequential impregnation. The reduced Ru/SiO_2 catalyst was impregnated with the cesium nitrate solution of the desired composition such that 2.2 ml solution per gram of support resulted in the appropriate Cs loading (Cs to Ru atomic ratios of 0.5, 1, 2 and 3). The promoted catalysts were dried in air at room temperature overnight and then at 383 K for 2 hours. These catalysts will be designated in the text as Cs#, where # is the Cs:Ru atomic ratio of the catalyst, e.g. Cs3 will be the catalyst with a Cs:Ru ratio of 3:1.

Thermogravimetric Analysis (TGA) Experiments

Thermogravimetric measurements of 20 mg catalyst samples were conducted in a Perkin Elmer TGA 7 analyzer interfaced with a PE-7500 computer for data acquisition and automatic control of the experiment. Experiments were done under a gas flow of 40 cc/min. Mass flow controllers were used to adjust the flow rate of

a 10% hydrogen, 90% helium mixture. Heating rates varied from 1 to 10 K/min

depending on the temperature response of the sample under study.

NMR Sample Preparation

About 100 mg of catalyst was placed in 5 mm O.D. NMR tubes and then

attached to sample ports of an adsorption apparatus described elsewhere (18). To

eliminate the moisture in the catalyst, the samples were heated to 423 K for 30

minutes in 760 torr of He. The samples were evacuated and dosed with

approximately 100 torr of hydrogen and the temperature was increased to 723 K at

a rate of 6 K/min. At this temperature, hydrogen was replenished every 30

minutes for 2 hours. After reduction, the samples were evacuated for 4 hours at

the reduction temperature and then allowed to cool to room temperature. Each

sample was then exposed to hydrogen at the desired pressure for 20 minutes

unless otherwise indicated. Finally, the samples were immersed in a water bath,

sealed with a microtorch, and weighed. When the strongly bound hydrogen on the

catalysts was investigated, the samples were dosed with hydrogen at 150 torr

equilibrated for 1 hour, evacuated to 10^{-5} torr for 5 minutes, sealed, and weighed.

NMR Experiments

A home-built spectrometer with ^{1}H resonance frequency of 220 MHz was

used for the NMR experiments. All proton NMR spectra of hydrogen-dosed

catalysts consisted of two peaks: one diamagnetic resonance associated with the

protons in the support and a second resonance representing hydrogen on the metal particles (18) with frequencies shifted upfield due to the Knight shift interaction between proton nuclear spins and metal conduction electrons. At a recycle time of 0.4 seconds the full recovery of the metal peak was established but the silanol peak intensity was suppressed because of its longer spin-lattice relaxation time. When the full intensity of the silanol peak was investigated, the recycle time was set at 50 seconds to achieve complete relaxation. The spin lattice relaxation times, T_1, of hydrogen on the metal were determined by the null point method (19). Absolute intensities were obtained by referring to a water sample doped with trace amounts of $FeCl_3$. The reference sample was sealed in a capillary tube of the length of the catalyst samples to account for field inhomogeneities in the NMR coil (18). All NMR measurements at this frequency were performed at 294±1 K.

In-situ ^1H NMR experiments were run in a home-built spectrometer operating at a proton resonance frequency of 250 MHz. The NMR probe, which was connected to a vacuum/dosing manifold, allowed temperatures up to ≈770 K and was operable in the pressure range from 4×10^{-6} to 10^3 torr. Sample reduction and pretreatment were carried out inside the probe following the procedure used for preparing the sealed NMR samples. Selective inversion of a narrow frequency band (hole burning) within the resonance line ascribed to hydrogen on Ru was achieved employing the DANTE technique (24). The rf pulse train consisted of 20

narrow pulses (pulse width $\approx$ 0.5 μs), separated by a μs delay, allowing selective

inversion of a frequency band of 2.5 KHz width.

RESULTS

The reduction temperatures of the catalysts were determined from TGA studies. The results of the thermogravimetric analyses are given in Table 1. In the presence of Cs promoters, the reduction temperature of the catalysts increased significantly.

The ^{1}H NMR spectra of an unpromoted catalyst under different hydrogen pressures are shown in Fig. 1. The upfield peak (-50 ppm) in each spectrum was identified as hydrogen dissociatively chemisorbed on ruthenium, and the downfield peak at ca. 3 ppm (diamagnetic peak) was assigned to the protons in the silica support (18). The upfield peak was best fit by an exponential Gaussian function, and for the peak at 3 ppm a superposition of one sharp Lorenzian and one broad Gaussian peak was used. The integrated intensity of the -50 ppm resonance was

Table 1. The effect of the Cs loading on the reduction temperature of the catalyst

Catalyst	Cs:Ru atomic ratio	$T_{red}(K)$
Ru10	0.0	433
Cs05	0.5	668
Cs1	1.0	635
Cs2	2.0	641
Cs3	3.0	621
30 wt% Cs	N/A	750
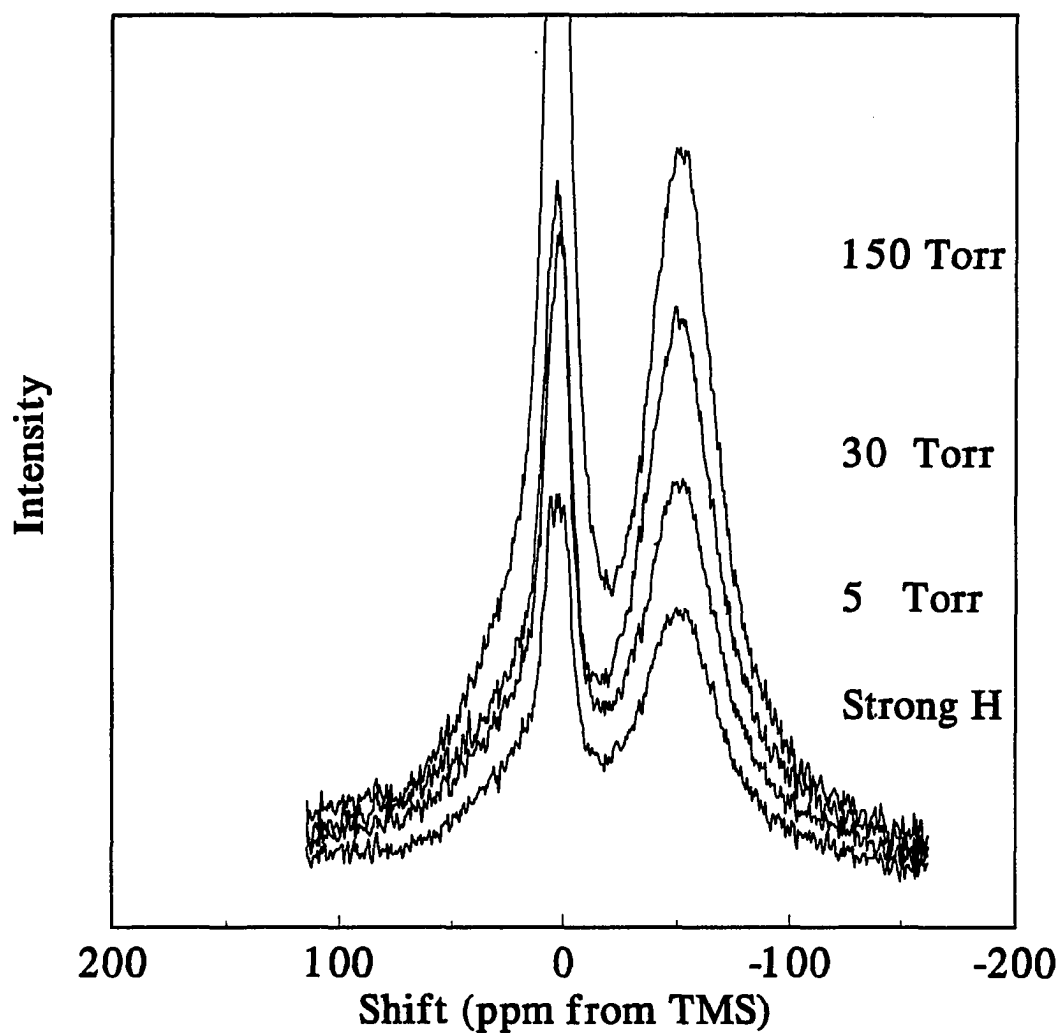
Figure 1. The NMR spectra of unpromoted 10% Ru/SiO_2 catalyst under different hydrogen pressures

used to obtain the H/Ru ratio as described in the methods section. As the hydrogen pressure was elevated, the H/Ru peak intensity as well as the intensity of the diamagnetic peak increased.

The NMR spectra for a Cs3 (Cs:Ru=3:1) under varying hydrogen pressures are shown in Fig. 2. The resonance shift of the H/Ru line was not influenced by the presence of Cs (see Table 2). However, a very sharp diamagnetic resonance at $\approx$ 3 ppm and a broad resonance at $\approx$ 10 ppm was observed. The broad line at $\approx$ 10 ppm exhibited a variation in intensity depending on pressure. Similar experiments were performed for the catalysts Cs05, Cs1 and Cs2.

The amount of hydrogen chemisorbed on the metal particles obtained from the integrated intensities of the corresponding resonance lines were normalized with respect to the line intensity originating from the strongly bound hydrogen adsorbed on the unpromoted catalyst and are plotted in Fig. 3. The amount of strongly bound hydrogen remains constant with increasing Cs loading, as shown in Fig. 4.

The hydrogen desorption isotherm was obtained for Cs3. Four samples were initially reduced and evacuated as described in the previous section, and dosed with 150 torr of hydrogen. After 2 hours, one sample was sealed. For the other three samples, the hydrogen pressure was reduced to 77 torr. The second sample was sealed after 12 hours of equilibration and the remaining 2 samples were evacuated to 30 torr and allowed to equilibrate for 14 hours before sealing the third
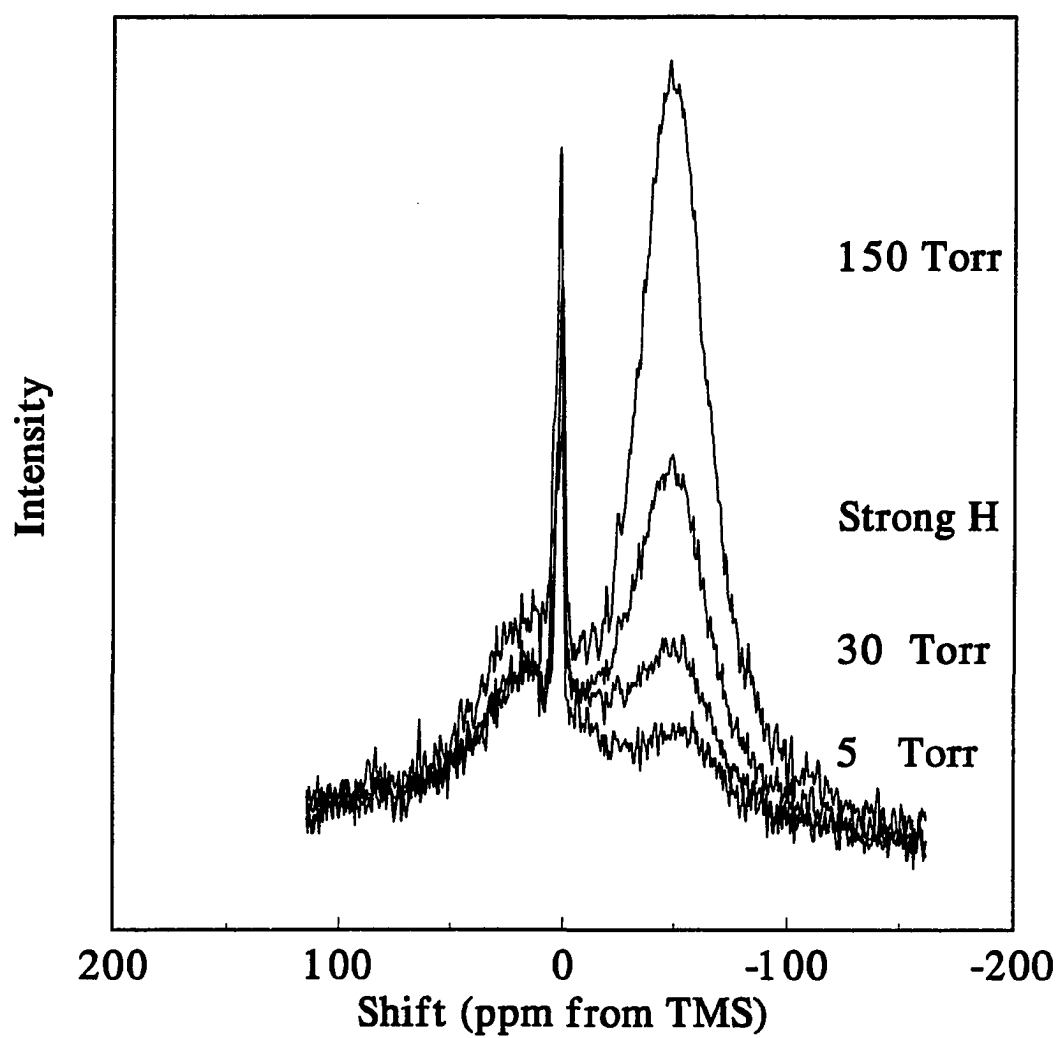
Figure 2. The NMR spectra of Cs promoted, 10% Ru/SiO$_2$ catalyst under different hydrogen pressures. Cs:Ru atomic ratio is 3
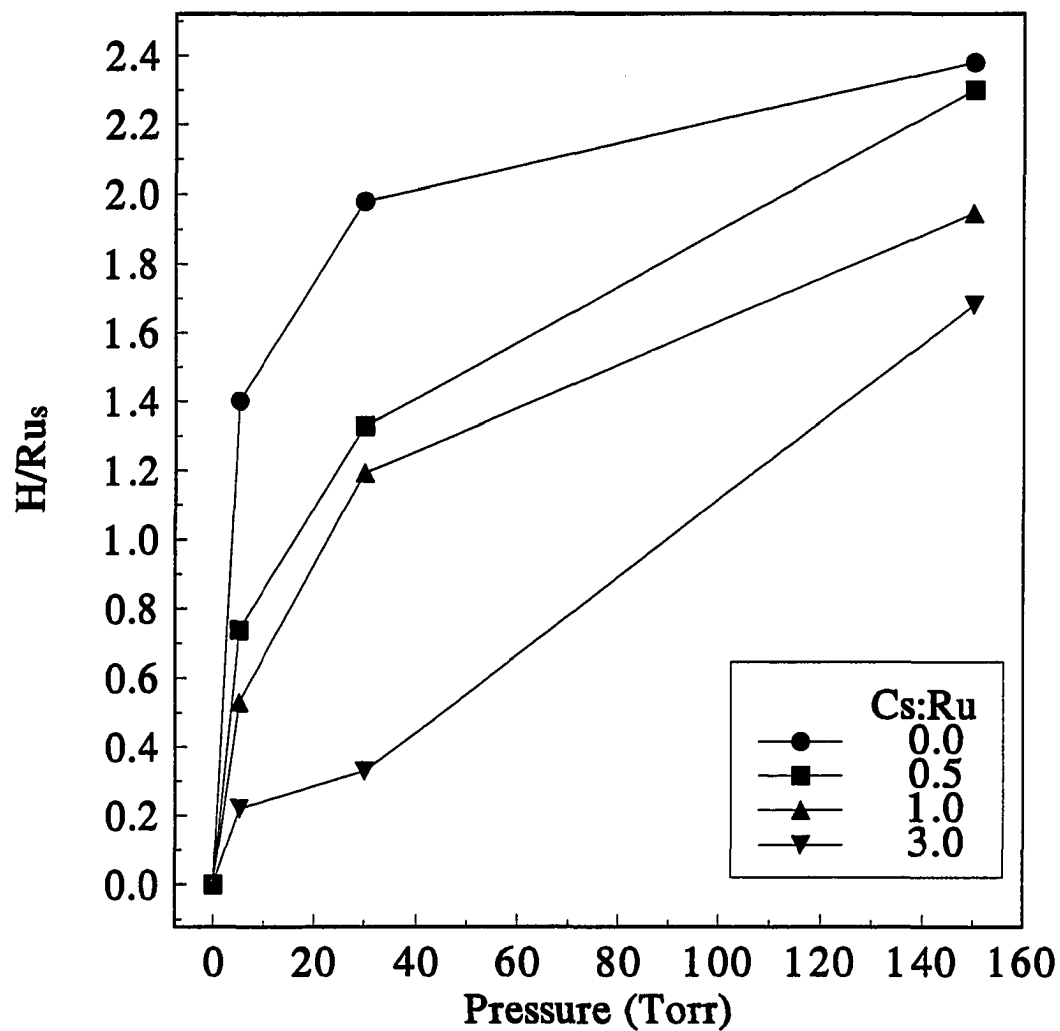
Figure 3. Hydrogen adsorption as a function of Cs loading and hydrogen
pressure. Hydrogen equilibration period was 20 minutes
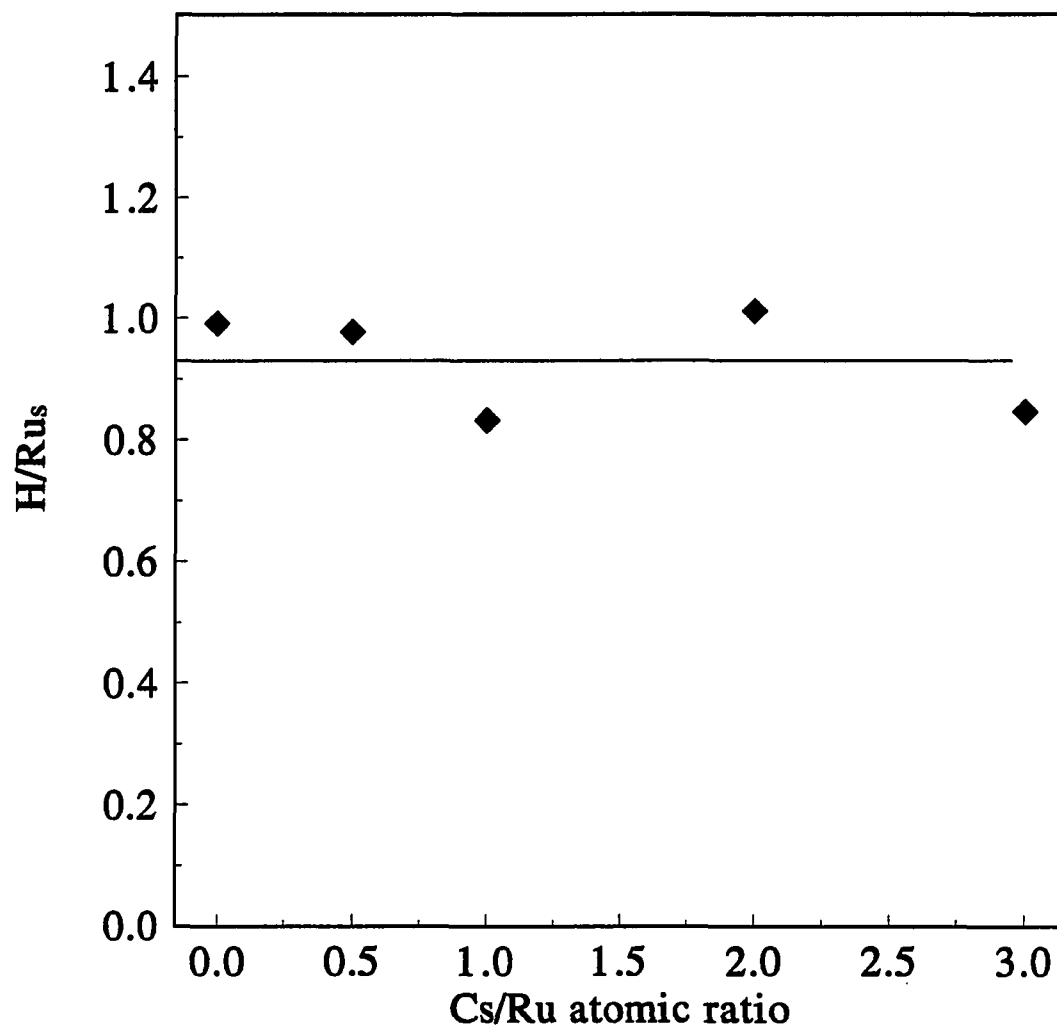
Figure 4. The effect of Cs loading on the amount of strongly bound hydrogen.
The samples were dosed with hydrogen at 150 torr before evacuation to
10^{-5} torr

Table 2. The effect of Cs on the Knight shift and the spin-lattice relaxation times of the strongly bound hydrogen

Catalyst	Knight Shift	T_1 (ms)
Ru10	52	65
Cs05	51	82
Cs1	48	100
Cs2	48	100
Cs3	48	100

sample. The hydrogen pressure of the last sample was then decreased to 5 torr and equilibration was allowed for 14 hours prior to sealing. The amount of hydrogen adsorbed on these catalysts (see Fig. 5) was determined from the integrated intensities of the NMR resonance lines at -50 ppm. The adsorption isotherm for the unpromoted catalyst (also shown in Fig. 5) coincides with this desorption isotherm.

During the same experiment, the effect of the hydrogen exposure times on the diamagnetic resonances were also monitored. It was noted that prolonged exposures of hydrogen influenced the downfield resonances 3 and 10 ppm, significantly (Fig. 6). The increase in the intensity of both resonances strongly depended on the hydrogen pressure, hydrogen exposure period and the Cs loading.
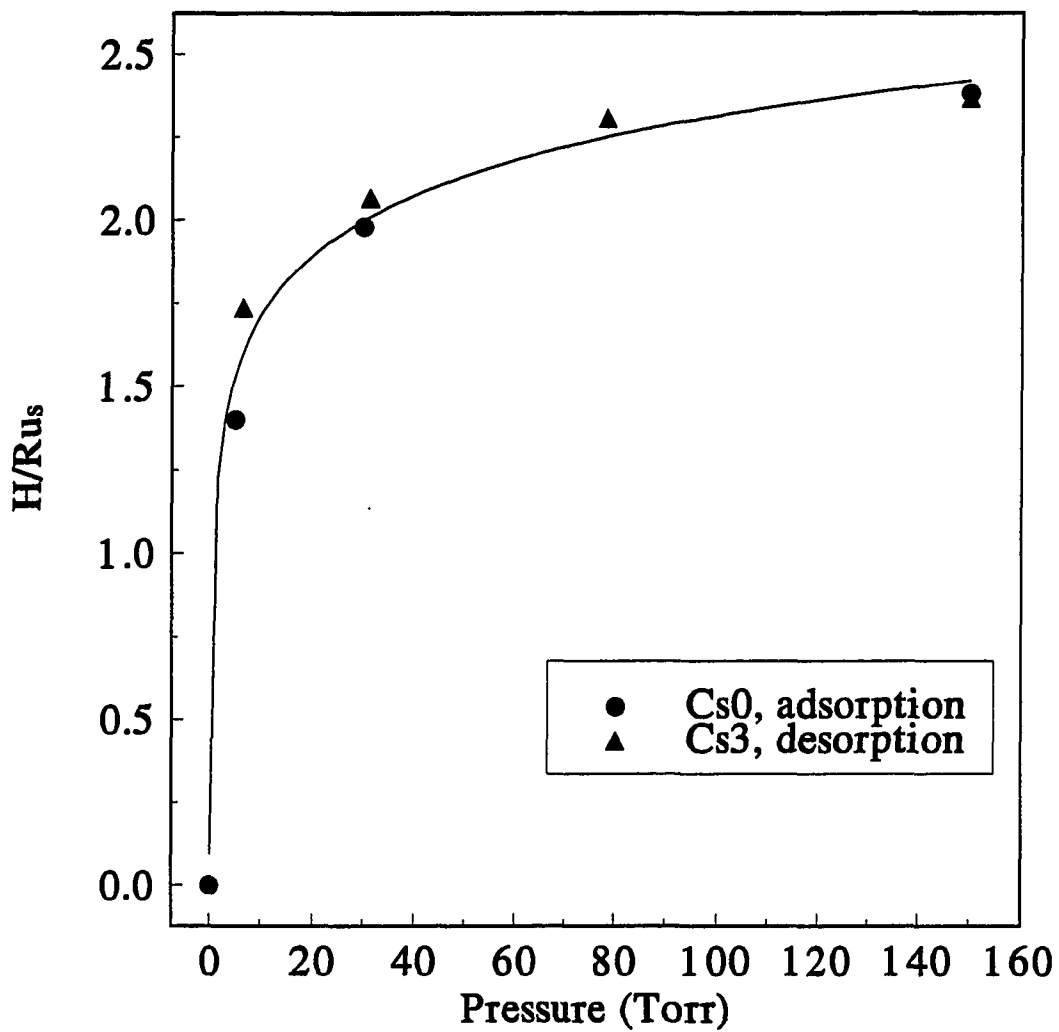
Figure 5. Desorption isotherm of the Cs promoted catalyst with a Cs:Ru atomic
ratio of 3:1. The solid circles correspond to the adsorption isotherm of
the unpromoted catalyst
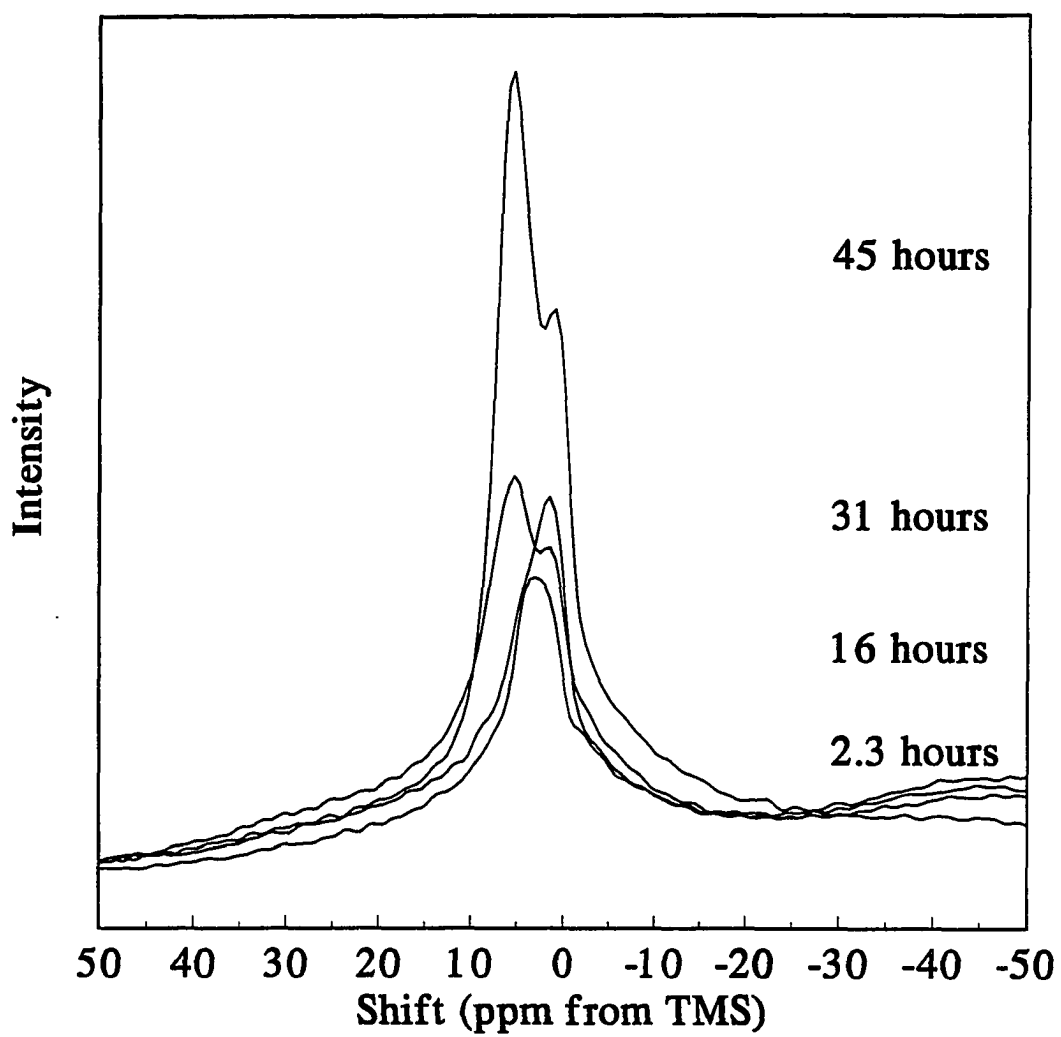
Figure 6. The effect of the spilled-over hydrogen on the downfield resonances

The remarkable agreement between the adsorption isotherm of the unpromoted catalyst and the desorption isotherm of Cs3 suggested the presence of a slow kinetic phenomenon in the presence of Cs promoter. The hydrogen adsorption isotherms of the promoted catalysts obtained after prolonged hydrogen exposures, at least 12 hours, (not shown) were found to agree very well with the adsorption isotherm of the unpromoted catalyst. All these data suggested that Cs no longer blocked hydrogen adsorption on the metal surface after long hydrogen exposures at room temperature.

In order to show that this effect was reversible upon desorption of hydrogen, three spectra were obtained. First, Cs3 was reduced and evacuated as described in the methods section. The first spectrum (Fig. 7 (a)) was taken after the sample was exposed to 30 torr of hydrogen for 20 minutes. After 18 hours of exposure spectrum (c) was obtained with a considerable increase of intensity for the peak ascribed to hydrogen on the metal. Spectrum (b) was taken after the same sample was evacuated at 383 K for 3 hours, cooled down to room temperature and dosed with 30 torr of hydrogen for 20 minutes. The variation of hydrogen-on-metal resonance with pretreatment suggested a partial recovery of the site blocking effect of Cs on hydrogen chemisorption.

The results presented here so far indicated the absence of both through metal electronic interactions and site blocking effects of Cs on Ru/SiO_2. The increase in the spin lattice relaxation times of adsorbed hydrogen as a function of Cs loading (Table 2) suggested the possibility that the hydrogen motion on alkali
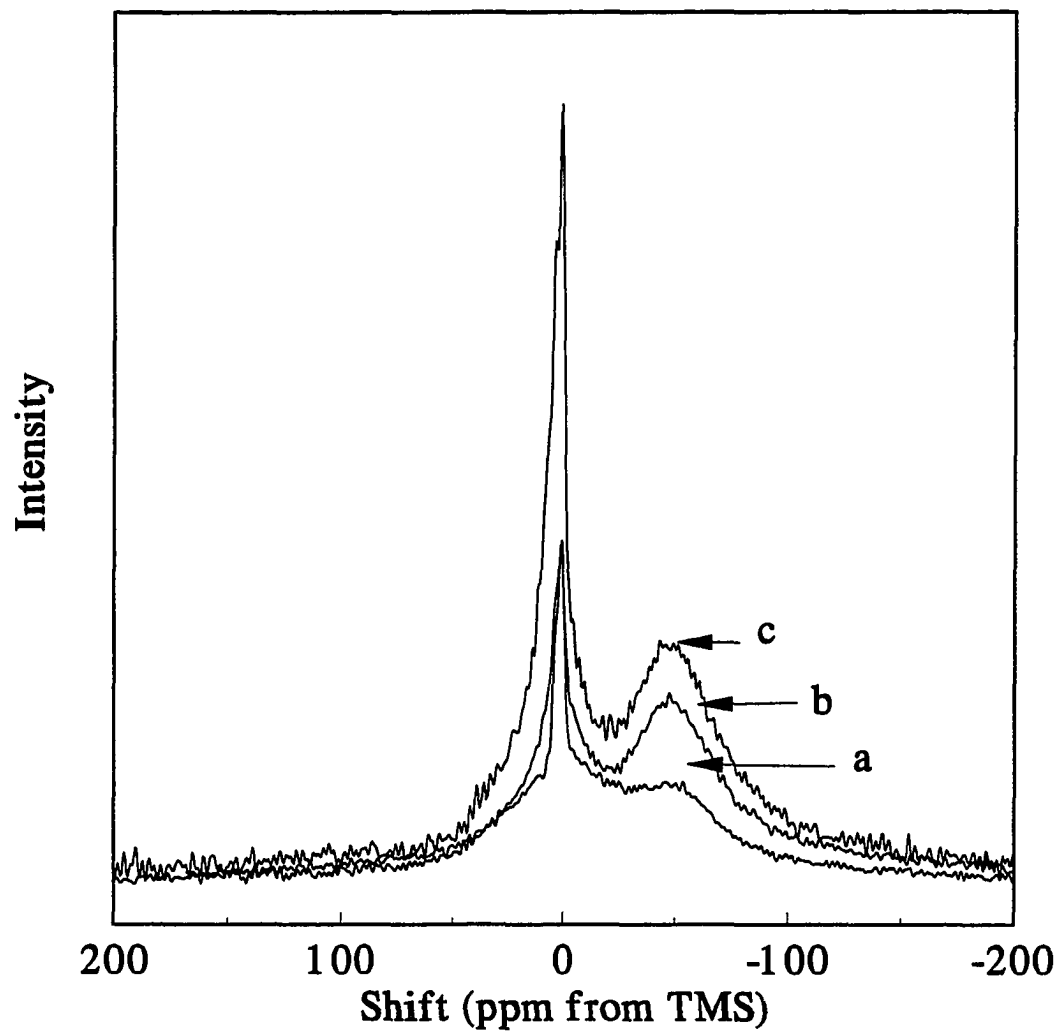
Figure 7. The response of a Cs:Ru=3 catalyst to different pretreatment procedures. For the details see the text

promoted surfaces may be altered. To test this hypothesis, selective excitation

(hole burning) measurements were performed at elevated temperatures and

pressures. It is well known that hydrogen on unpromoted Ru catalysts is

characterized by a high degree of mobility (18). As demonstrated in Fig. 8 it was

possible to selectively invert a narrow frequency band within the H/Ru peak (hole-

burning experiment) for an unpromoted and evacuated Ru/SiO_2 catalyst at room

temperature, which indicated that the H/Ru peak is inhomogeneously broadened

under these conditions. Elevation of the hydrogen pressure to $\approx$ 0.5 torr led to

disappearance of the H/Ru peak, when the same excitation conditions were

applied (Fig. 8, upper spectrum), giving evidence that the H/Ru line became

homogeneously broadened. Hole-burning NMR experiments performed with the

Cs3 promoted catalyst revealed a completely different behavior (Fig. 9). Even at

high hydrogen pressures (735 torr) and elevated temperatures (533 K), as shown

in the lower part of Fig. 9, it became evident that the H/Ru resonance line remains

inhomogeneously broadened.
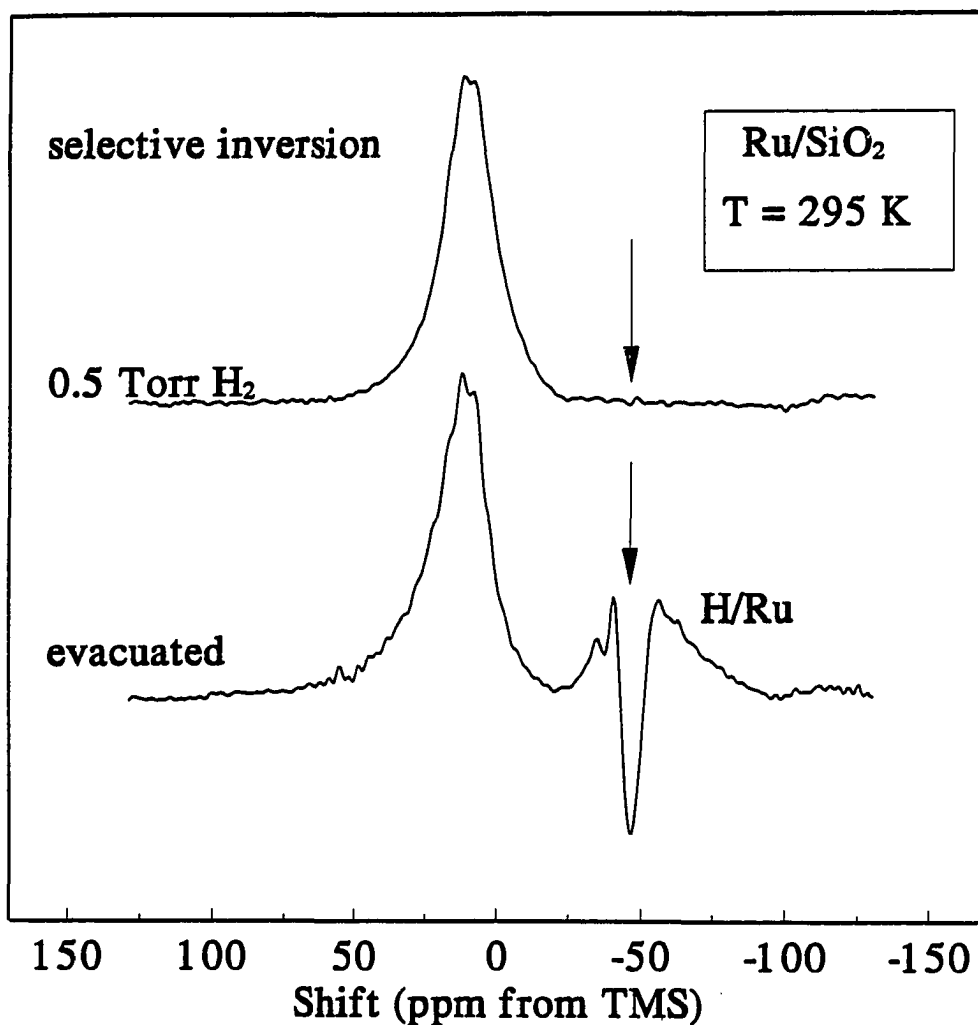
Figure 8. Selectively excited ^{1}H NMR spectra of unpromoted Ru/SiO$_2$ (Ru loading 4%). Bottom: evacuation conditions (5 × 10^{-6} Torr), revealing inhomogeneous line-broadening as main mechanism for the H/Ru line-shape. Top: disappearance of the H/Ru peak under selective-excitation at a hydrogen pressure of 0.5 torr, indicating homogeneous line-broadening. The arrows indicate the position of the rf-carrier frequency.
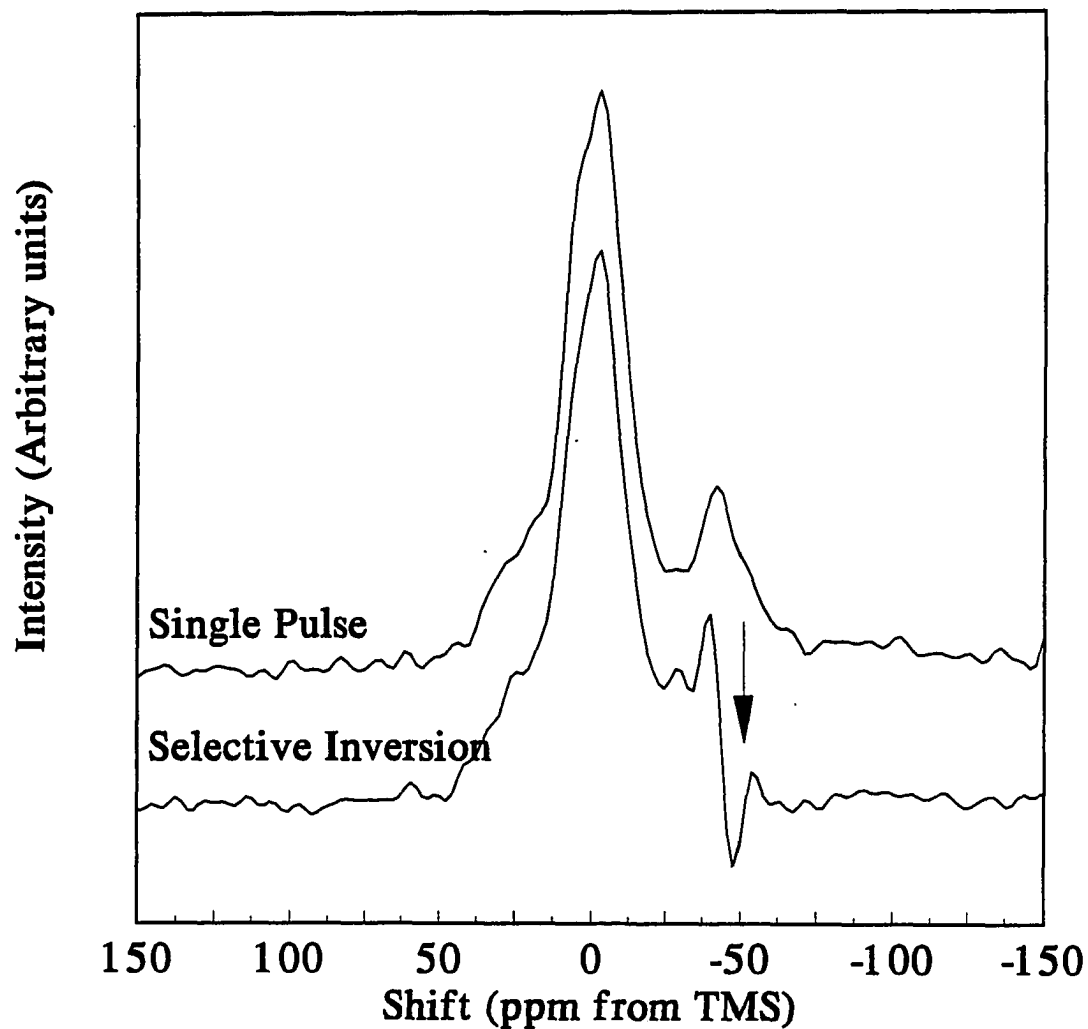
Figure 9. Nonselectively excited (top) and selectively excited ^{1}H NMR spectrum (bottom) of a catalyst containing Cs (Cs:Ru = 3) at 533 K and a hydrogen pressure of 735 torr. The arrows indicate the rf carrier frequency. The selectively inverted intensity in the bottom spectrum (marked by an arrow) within the resonance ascribed to hydrogen on the metal indicates that this resonance is mainly inhomogeneously broadened.

DISCUSSION

The reduction temperatures of the catalysts increased as a function of Cs

loading (Table 1) as indicated by the TGA studies. The same effect was also

observed for K promoted Ru/SiO_2 catalysts (8). It is worth noting that both the

metal and the promoter precursors reduced simultaneously. This result indicated

that both precursors interacted intimately during the reduction. However, the Cs

compound formed after reduction ($CsO_{x=1,2}$) was not capable of donating electrons

to the metal substrate. The Cs-O coadsorption studies on Ru(0001) single crystals

have shown that Cs transferred its charge to oxygen not to the metal surface (20).

The absence of Knight shift changes (Table 2) is consistent with this finding.

The hydrogen-on-metal (-50 ppm) resonance intensities were smaller for

samples under 5 and 30 torr of hydrogen than the intensity of the same resonance

on the sample evacuated to 10^{-5} torr for 5 minutes after hydrogen exposure at

150 torr. This behavior was reflected in the hydrogen adsorption isotherms (Fig.

3). Also, the isotherms merged at a hydrogen pressure of 150 torr. After

evacuation, all of the samples had the same strong hydrogen-to-ruthenium ratio

irrespective of the Cs loading (Fig. 4) suggesting that Cs lost its site blocking

character after extended exposures to hydrogen. When the hydrogen exposure

times were increased to at least 12 hours, essentially identical adsorption

isotherms were obtained for unpromoted and promoted catalysts (not shown).

Similarly, the desorption isotherms for the promoted catalysts were exactly the

same as the adsorption isotherms of the unpromoted catalysts (Fig. 5). The results given in Fig. 7 indicated that the Cs promoter could again block hydrogen adsorption sites after thermal treatment in vacuum. All these findings suggest that Cs behaves as if it is pushed off the metal particles by prolonged exposure to hydrogen and migrate back to the metal after hydrogen desorbs. However, the possibility that hydrogen slowly diffuses under the Cs overlayer can not be excluded. This is in contrast to the site blocking effect observed with other alkali promoters (7-8, 23).

The NMR spectra in Figs. 1 and 2 show that the intensity and the linewidth of the resonance lines due to the hydrogen in the support decreased in the presence of Cs. The excess amount of Cs on the support surface led to a considerably diminished hydrogen spillover occuring during short (½ to 1 hours) exposures. However, some hydrogen spillover took place on promoted catalysts during extended periods of hydrogen exposure as shown by increased intensities of both diamagnetic (3 ppm and the 10 ppm) resonances increased significantly (Fig. 6). Most likely CsOH or CsH species are formed in the presence of spilled over hydrogen.

Cs promoters are reported to be superior to Na or K promoters on supported metal catalysts in ammonia and Fischer-Tropsch syntheses (5, 22). Our results indicated that at room temperature, Cs is pushed off the surface of the metal (or loses its site blocking ability) while no such effect has been observed for Na- and K-promoted Ru/SiO_2 catalysts (8, 23). Since this work for Cs, and previous work

for Na and K promoted Ru/SiO$_2$ catalysts (8, 23) show that the through-metal electronic interactions are not observed (Knight shift does not vary with the alkali content), and the site blocking effect is not operable for the Cs promoted catalysts, the question of the role of the alkali promoters arises. The first important effect reported here is the decrease in the amount of spilled-over hydrogen with Cs loading, most likely originating from restricted mobility of hydrogen at the interface between metal particles and the support. Secondly, the hole-burning experiments showed a change in the mobility of hydrogen interacting with the Ru particles in the case when Cs is present. The fact that the H/Ru resonance line of Cs promoted Ru catalysts is inhomogeneously broadened at high temperatures and hydrogen pressures implies that: (i) direct dipolar couplings among proton spins are negligible and do not account for the line broadening mechanism, and (ii) hydrogen motion does not lead to a homogeneous H/Ru line shape as observed for unpromoted Ru/SiO$_2$ catalysts. From (i) it follows, that hydrogen in the Cs promoted catalyst has to be regarded as mobile, otherwise dipolar couplings would not be averaged out and would yield increased line widths at elevated pressures (18d). From (ii) it can be concluded, however, that the motion of hydrogen in Cs promoted Ru/SiO$_2$ catalysts is different from the type of motion which hydrogen undergoes in non-promoted Ru/SiO$_2$ catalysts. In the latter case, the H/Ru peak becomes homogeneously broadened already at hydrogen pressures as low as 0.5 torr and at room temperature, which leads to an intensity decrease or even disappearance of the whole resonance line under selective-excitation conditions

(Fig.8 top), depending on the specific parameters of the rf-pulse sequence. For the unpromoted Ru/SiO_2 catalyst the transition from an inhomogeneously broadened to a homogeneously broadened line can be explained by a model, which derives the NMR line shape under selective-excitation conditions (25). The model describes an exchange process of hydrogen, originating from adsorption/desorption involving hydrogen diffusion on the surface of Ru particles For the Cs-promoted catalyst the situation is more difficult to interpret, because it is not known whether the inhomogeneously broadened NMR line results from a superposition of narrow resonances originating from hydrogen adsorbed on different Ru particles, or from hydrogen adsorbed on various sites or regions of one Ru particle. It can be concluded, that the nature of hydrogen motion must be significantly different compared to unpromoted Ru/SiO_2, although we have not identified which motional degrees of freedom become restricted by the presence of Cs.

It is postulated, that the modified character of hydrogen mobility in the presence of the Cs promoter can explain its role in the Fischer-Tropsch synthesis. The chain termination in Fischer-Tropsch synthesis takes place by hydrogen abstraction or addition to form olefins and paraffins, respectively. Therefore, an increase in the chain growth probability of the Fischer-Tropsch synthesis in the presence of the alkali promoters can be attributed to the hydrogen deficiency on the metal surfaces. Since the amount of hydrogen on the Cs promoted catalysts does not change with Cs coverage, one can argue that the availability of hydrogen in the vicinity of the growing hydrocarbon chains depends on particle-surface diffusion

or the dynamics of hydrogen due to adsorption/desorption. In addition, other promotional effects such as higher olefin/paraffin ratios and increase in CO_2 production are also consistent with this observation of modified hydrogen mobility.

CONCLUSIONS

The promotional effects of Cs on Ru/SiO_2 catalysts were studied via ^1H NMR spectroscopy. There was no evidence of a ruthenium-mediated electronic interaction between the Cs promoter and adsorbed hydrogen at least as indicated by the proton Knight shifts. The site blocking effect of Cs was not as significant as that of Na or K promoters. After exposure to hydrogen for extended periods of times, the site blocking effects of the Cs promoter diminished. This effect was reversible after thermal evacuation of the hydrogen. In the presence of Cs, the surface of the support was also modified. Because of the ion exchange between the silanol protons in the silica support and the Cs promoter, the intensity of the diamagnetic resonance in the spectrum decreased. Also an additional resonance associated with the Cs species in the support appeared in the spectra. The mobility of the hydrogen on the Ru surface and at the metal-support interface (spillover) was restricted in the presence of Cs. The restricted mobility of hydrogen can qualitatively explain the promotional effects of alkali promoters on the Fisher Tropsch synthesis reaction.

ACKNOWLEDGEMENTS

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PAPER 3.   EFFECT OF Na PROMOTERS ON THE MOBILITY OF HYDROGEN
CHEMISORBED ON Ru/SiO$_2$ SURFACES

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ABSTRACT

The role of Na promoters in the interaction between hydrogen chemisorbed on Ru/SiO$_2$ catalysts was investigated via ^{1}H NMR spectroscopy. No evidence was found for a Ru mediated electronic interactions between Na promoter and the chemisorbed hydrogen. Na promoter blocked available hydrogen chemisorption sites on the Ru surface as monitored via proton spin counting the hydrogen on the metal resonance. Dynamic studies performed via selective saturation ^{1}H NMR spectroscopy indicated that the mobility of hydrogen on the metal surface was significantly restricted in the presence of Na promoters.

INTRODUCTION

Alkali metal promoted catalysts are widely used in Fischer Tropsch synthesis and ammonia synthesis reactions. In the Fischer Tropsch synthesis reaction, alkali promoters are reported to (i) enhance the rate of CO consumption, (ii) enhance the chain initiation and propagation, (iii) supress methane formation, and (iv) increase the olefin content of the reaction products (5). In the ammonia synthesis reaction, the catalytic activity of supported or unsupported Ru is reported to increase with a decrease in the ionization potential of the added alkali promoter (Cs>K>Na) (6). The existing theories for these and other effects of alkali species include active metal site blocking for chemisorption, electron donation to or from the metal, direct chemical interactions between adsorbate and the promoter, through-space interactions (e.g., electrostatic), and alkali-induced surface reconstruction. The promoters can also stabilize the ionic forms of the active metals, M^+, which are the active centers for oxygenate formation (13), and protect these against reduction (Madelung stabilization). In addition, alkali promoters can chemically interact with the oxide supports to change their acidity (14) or form chemically distinct, highly mobile species (15). A more general review of these mechanisms can be found elsewhere (1).

In addition to these mechanisms, Laser Induced Thermal Desoprtion (LITD) studies on sulfur covered Ru(001) indicated a decrease in the hydrogen diffusion coefficient with increasing sulfur coverage (20). Sulfur induced decrease in the

diffusion coefficient of hydrogen was contained in the preexponential of the

hydrogen surface diffusion coefficient but not in the activation barrier of diffusion.

Since the presence of sulfur and the alkali promoters have similar effects on the

Fischer Tropsch synthesis a similar phenomenon may prevail in the latter case as

well.

^{1}H NMR spectroscopy has been successfully used to characterize

unpromoted and promoted supported metal catalysts (1-3). The quantitative

nature of the technique was used to investigate the site blocking effects of the

alkali promoters. The electronic interactions between the alkali promoter and the

Ru metal surface was monitored via the changes in the frequency of the hydrogen-

on-metal resonance which was due to the changes in the density of states at the

metal Fermi level (Knight shift). The selective saturation experiments were used to

elucidate the heterogeneity of the hydrogen environment as a function of the

temperature and the pressure. The results were interpreted in terms of the effect

of the Na on the mobility of the adsorbed hydrogen.

METHODS

Catalyst Preparation

All catalysts in this study were prepared via incipient wetness. The Na promoted catalysts were prepared via a sequential and a co-impregnation technique. To prepare sequentially impregnated catalysts, a sufficient amount of ruthenium nitrosyl nitrate (Johnson Matthey) was dissolved in 2.2 ml water/g of support to yield a metal loading of 4 wt% in the reduced catalyst. Then a slurry was prepared by mixing an appropriate amount of silica (Cab-O-Sil HS-5) in the ruthenium nitrosyl nitrate solution and dried overnight at room temperature and then for 4 hours in air at 383 K. The unpromoted catalyst was reduced in flowing hydrogen for 2 hours at 623 K. The reduced Ru/SiO_2 catalyst was impregnated with the sodium nitrate (Johnson Matthey) solution of the desired composition such that 2.2 ml solution per gram of support resulted in the appropriate Na loading. The promoted catalysts were dried in air at room temperature overnight and then at 383 K for 2 hours. The co-impregnation solution was prepared by dissolving an appropriate amount of sodium nitrate in the ruthenium nitrosyl nitrate solution obtained from Strem Chemicals (1.5 wt%). The support was impregnated with the solution and dried. An unpromoted catalyst was also prepared from the same precursor. All of the catalysts had a final Ru loading of 4 wt%.

A Na promoted catalyst was also prepared from a ruthenium nitrosyl nitrate salt obtained from Johson Mathey. Elemental analysis by atomic absorption

spectroscopy indicated that this precursor contained 10.7 wt% Na which corresponded to a Na:Ru atomic ratio of 1.75:1. An 8% and a 10 wt% Ru/SiO_2 catalyst were also prepared by incipient wetness technique from this precursor.

NMR Sample Preparation

About 100 mg of catalyst was placed in 5 mm O.D. NMR tubes and then attached to sample ports of an adsorption apparatus described elsewhere (18). To eliminate the moisture in the catalyst, the samples were heated to 423 K for 30 minutes in 760 torr of He. The samples were evacuated and dosed with approximately 100 torr of hydrogen and the temperature was increased to 623 K at a rate of 6 K/min. At this temperature, hydrogen was replenished every 30 minutes for 2 hours. After reduction, the samples were evacuated for 4 hours at the reduction temperature and then allowed to cool to room temperature. Each sample was then dosed with hydrogen and equilibrated overnight. Finally, the samples were immersed in a water bath, sealed with a microtorch, and weighed. When the strongly bound hydrogen on the catalysts was investigated, the samples were dosed with hydrogen at equilibrated overnight, evacuated to 10^{-5} torr for 5 minutes, sealed, and weighed.

NMR Experiments

A home-built spectrometer with ${}^1H$ resonance frequency of 220 MHz was used for the NMR experiments on the sealed samples. All proton NMR spectra of

hydrogen-dosed catalysts consisted of two peaks: one associated with the silanol protons from the support and the other representing the hydrogen on the metal particles (18). At a recycle time of 0.4 second, the full recovery of the metal peak was established but the silanol peak intensity was suppressed because of its longer spin-lattice relaxation time. When the full intensity of the silanol peak was investigated, the recycle time was set at 50 seconds to achieve complete relaxation. The spin lattice relaxation times, T1, of hydrogen on the metal were determined by the null point method (19). Absolute intensities were obtained by referring to a water sample. The reference sample was sealed in a capillary tube of the length of the catalyst samples to account for field inhomogeneities in the NMR coil (18). All NMR measurements were performed at 294 ± 1 K.

The dynamics of hydrogen was investigated *in-situ* in another home built spectrometer with a ^{1}H resonance frequency of 250 MHz. The catalyst reduction was carried out *in-situ* in a home built probe operating between 100-773 K which was attached to a glass manifold with an operating pressure range of 10^{-6} - 10^3 torr. The same procedure used to prepare the sealed NMR samples was followed for the catalyst pretreatment. The *in-situ* measurements were carried out over a pressure range of 10^{-5}-760 torr and a temperature range of 294-700 K.

RESULTS

The ^{1}H NMR spectra of strongly bound hydrogen in a series of co-impregnated, sodium-promoted catalysts are shown in Fig. 1. The upfield peak (-60 ppm) in each spectrum was identified as hydrogen dissociatively chemisorbed on ruthenium and the downfield peak (3 ppm) was assigned to the silanol protons (2). The upfield peak was best fit by an exponential Gaussian function and for the peak at 3 ppm a superposition of one sharp Lorenzian and one broad Gaussian peak was used. The electronic interactions between the Na promoter and the chemisorbed hydrogen was monitored via the [1]H Knight shifts of the hydrogen-on-metal resonance. As seen in Fig. 1, the shift in the hydrogen-on-metal resonance did not change with alkali loading. The same behavior was observed for the sequentially impregnated catalysts as well (not shown).

The effect of Na promoter on the number of available hydrogen chemisorption sites on Ru was also monitored via ^{1}H spin counting of the hydrogen-on-metal resonance. The quantitative information was extracted by comparing the integrated hydrogen-on-metal resonance intensity with a water reference of known spin count. In Fig. 2, the change in the hydrogen-on-metal intensity was plotted against alkali loading for both sequentially and co-impregnated catalysts. The results were compared with a theoretical one-to-one site blocking case as indicated by a dashed line in the same figure. In addition to the intensity of the
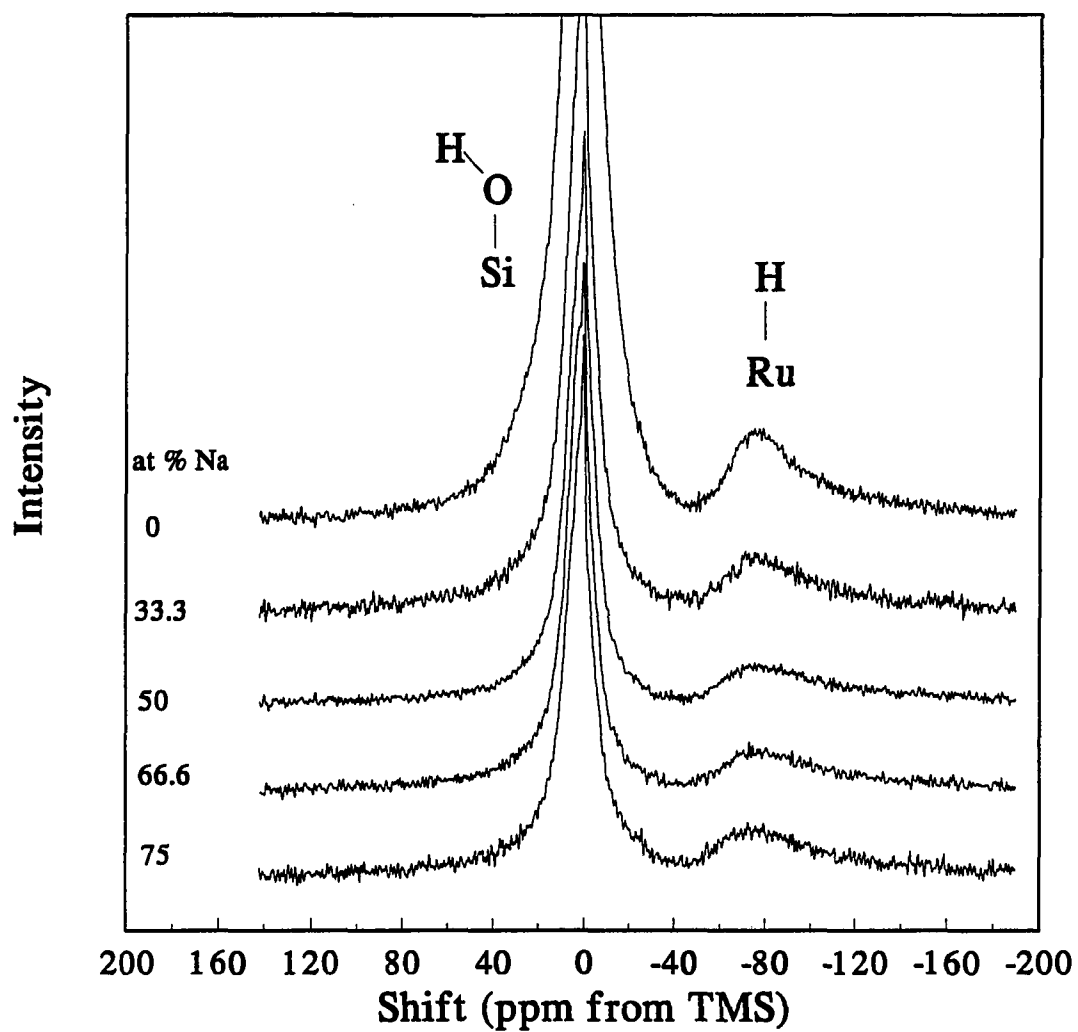
Figure 1. ^1H NMR spectra of co-impregnated $Na/Ru/SiO_2$ catalysts. Each of the spectra shown is obtained by averaging 1000 scans
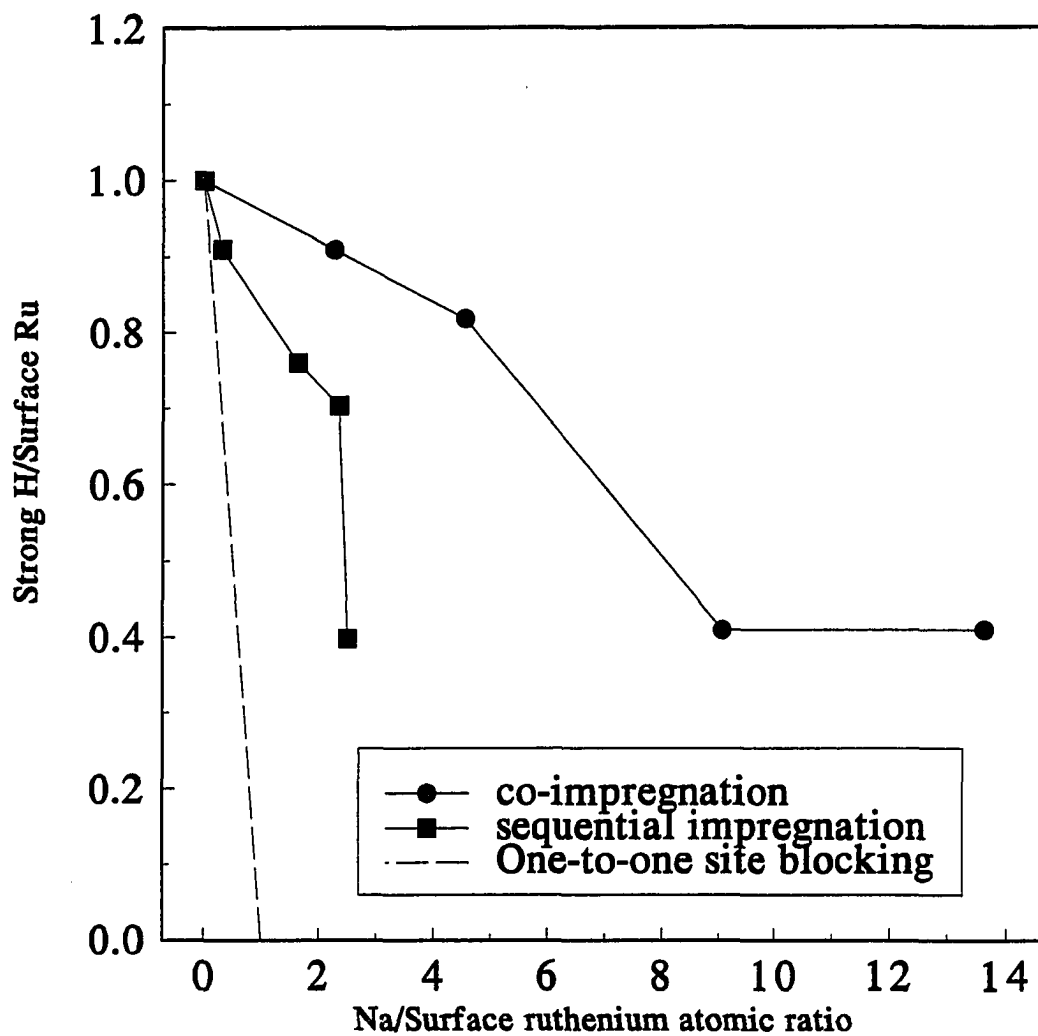
Figure 2. The site blocking effects of the Na promoter on the Ru/SiO$_2$ catalysts

hydrogen-on-metal surfaces, the presence of Na also influenced the intensity of the hydrogen in the support resonances as well. The intensity of the 3 ppm resonance decreased with increasing alkali loading. The effect of Na loading and the preparation technique on the hydrogen-in-support resonance was plotted in Fig. 3.

The presence of Na promoters decreased the amount of the weakly bound hydrogen states significantly. For example, the weakly bound β state present on unpromoted catalysts (16, 17) was not observed on the Na promoted catalysts (Fig. 4). The β state of hydrogen is structure sensitive, and its population depends very strongly on the density of the defect like sites present on the metal surface. Furthermore, the β state observed on unpromoted Ru/SiO_2 catalysts was in fast exchange with the mobile α and gas phase hydrogen (17), the absence of it also suggested that the presence of the Na promoter may have influenced the dynamics of chemisorbed hydrogen on the metal surface.

The dynamics of chemisorbed hydrogen was investigated by selective saturation (hole burning) measurements on an unpromoted and a Na promoted catalyst from the co-impregnated catalyst series. Part of the (-50) ppm resonance was excited with a comb of 20 short pulses (19) which was followed by a $\pi/2$ detection pulse (Fig. 5). The effect of temperature, pressure and the presence of Na on the dynamics of the chemisorbed hydrogen was monitored in terms of the parameters (area and the width) of the "hole" created in the -50 ppm resonance.
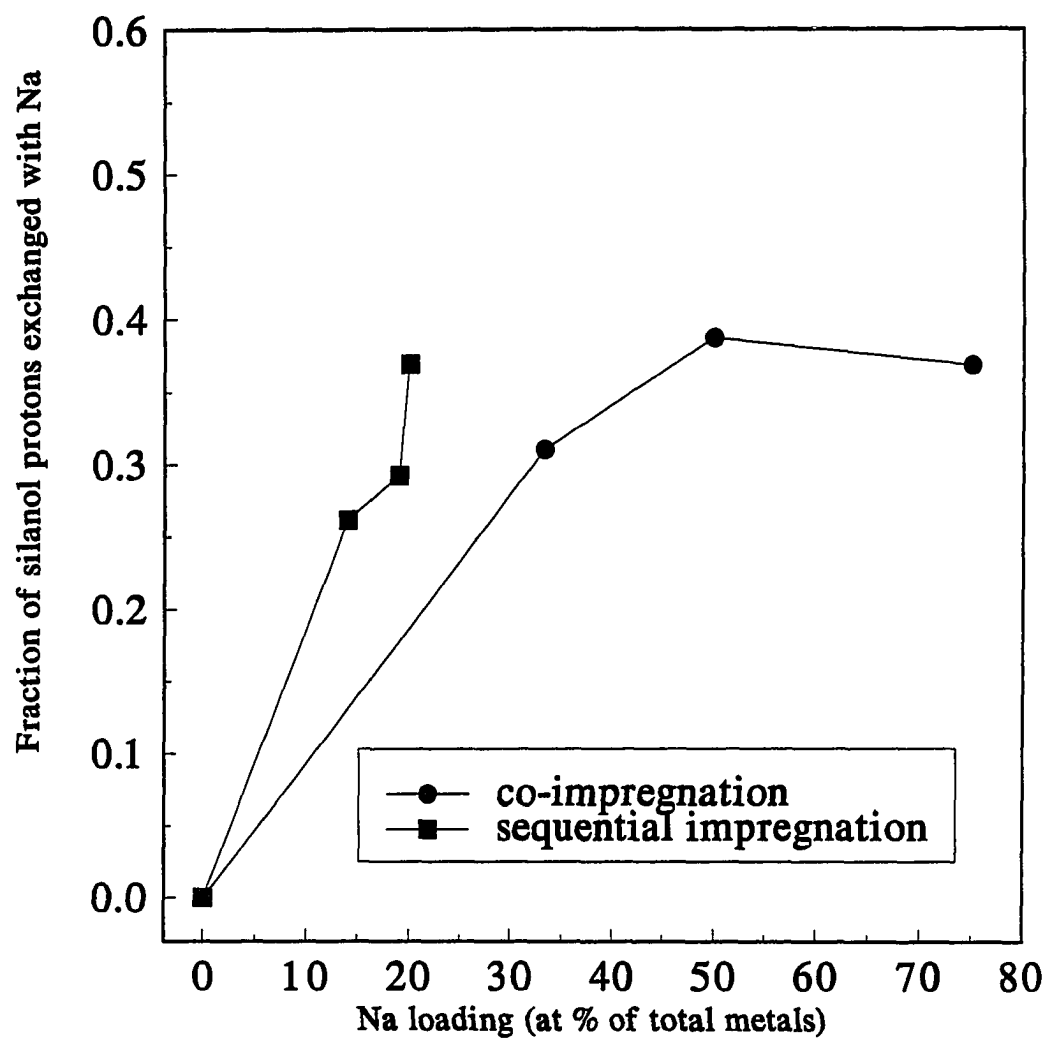
Figure 3. Effect of Na on the OH group intensities

The NMR spectra obtained after a single $\pi/2$ excitation was shown in Fig. 6 for an unpromoted catalyst. The selective excitation measurements done on the same sample under similar conditions are shown in Fig. 7. Similar measurements done on a Na promoted catalyst with a Na:Ru atomic ratio of 1.75 and a Ru loading of 8 wt% indicated that the -50 ppm resonance was heterogeneously broadened at higher pressures (200 torr) and higher temperatures (up to 500 K) (Figs. 8 and 9).
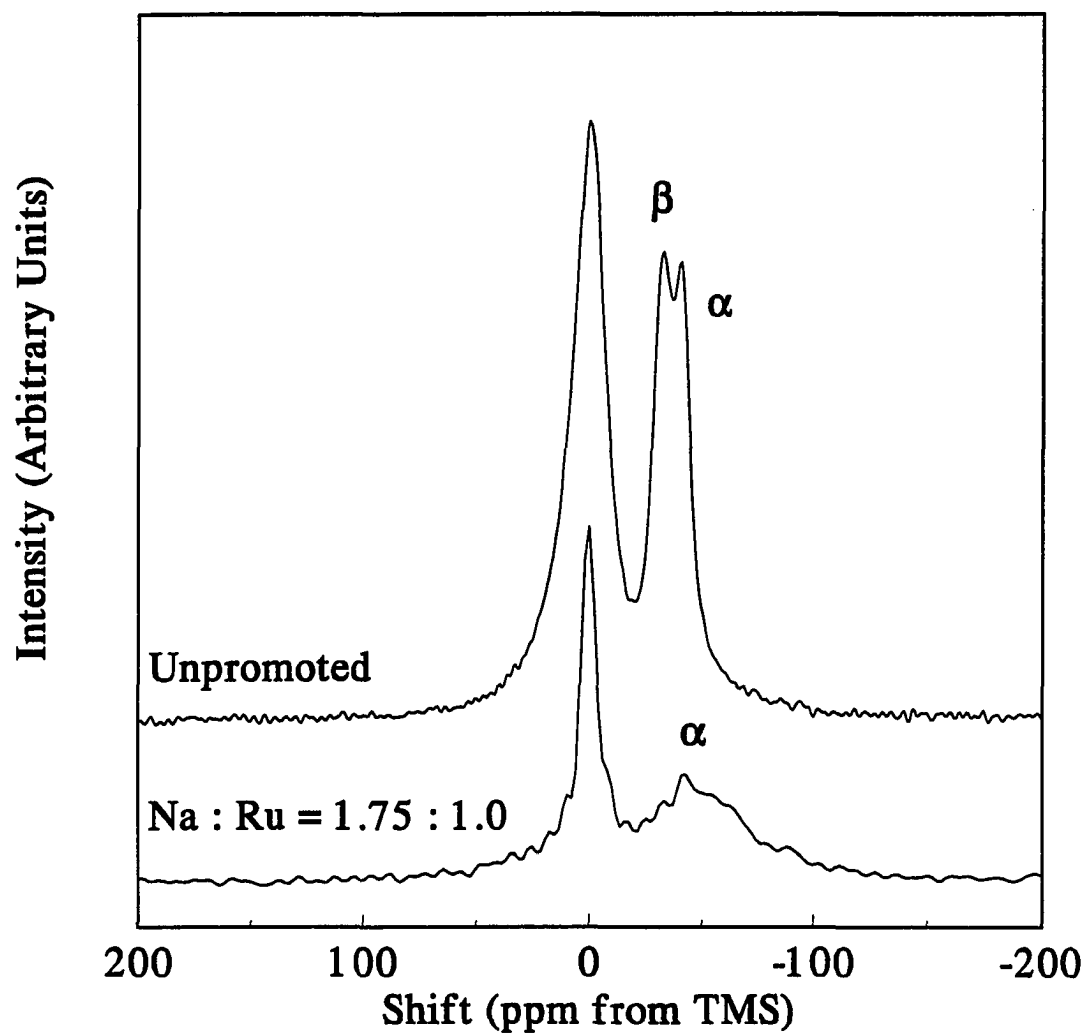
Figure 4. The effect of the Na promoter on the α and β states of the chemisorbed hydrogen
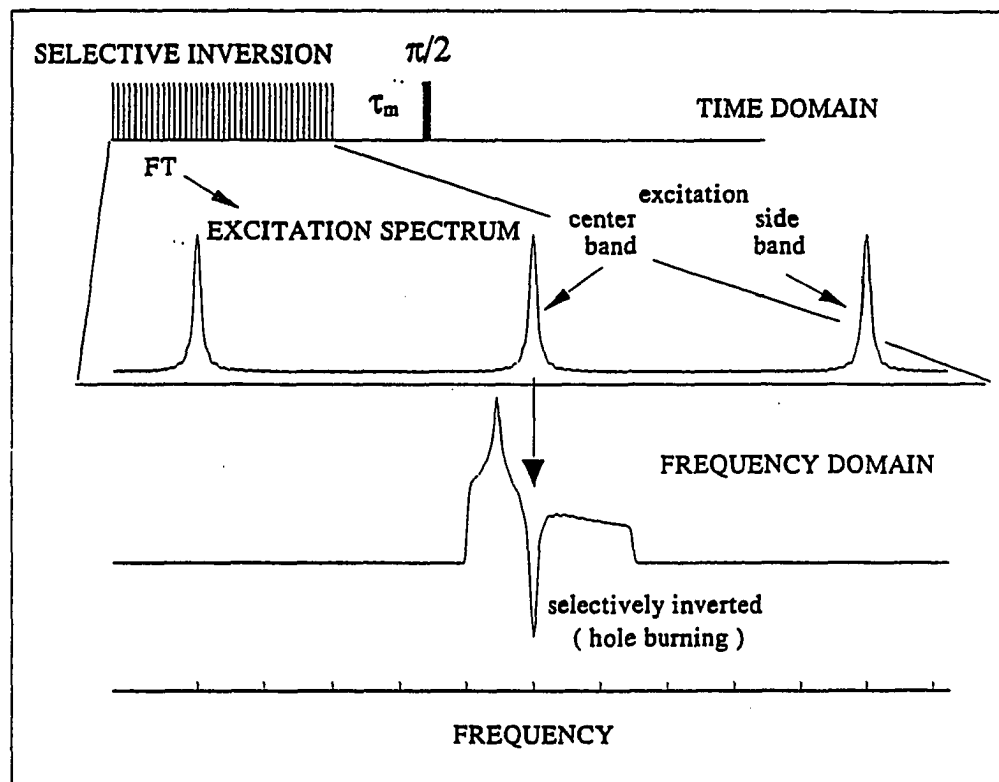
Figure 5. The pulse sequence used for the selective saturation measurements

H/Ru/silica, 293K

NHB

0.5 Torr H2

0.05 Torr H2

vacuum

300.0   200.0   100.0   0.0   -100.0   -200.0   -300.0   -400.0

ppm
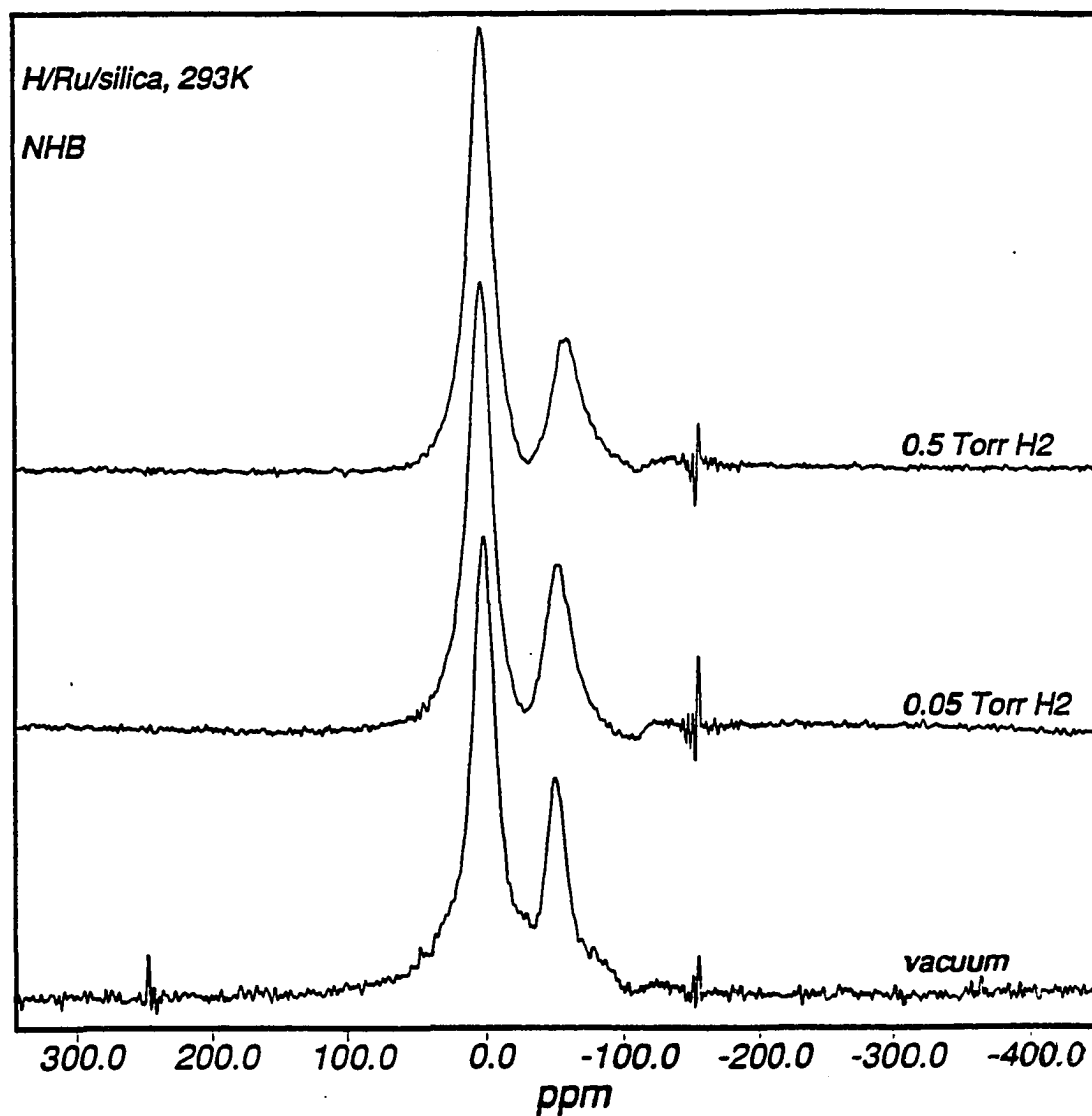
Figure 6. The hydrogen-on-metal resonance of 4%Ru/SiO$_2$ as a function of hydrogen pressure, single excitation spectra
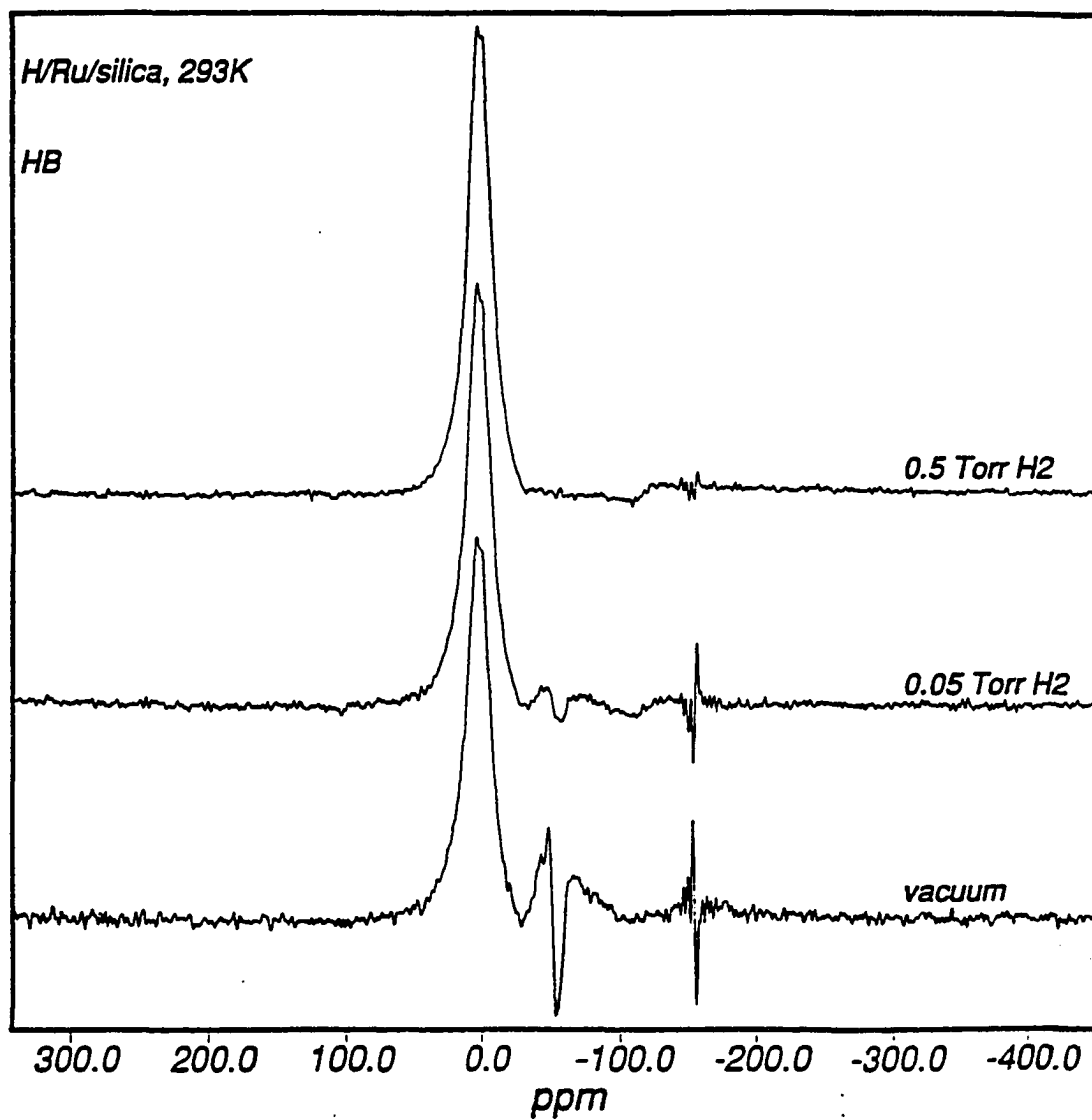
Figure 7. The hydrogen-on-metal resonance of 4%Ru/SiO₂ as a function of hydrogen pressure, -60 ppm resonance was selectively inverted
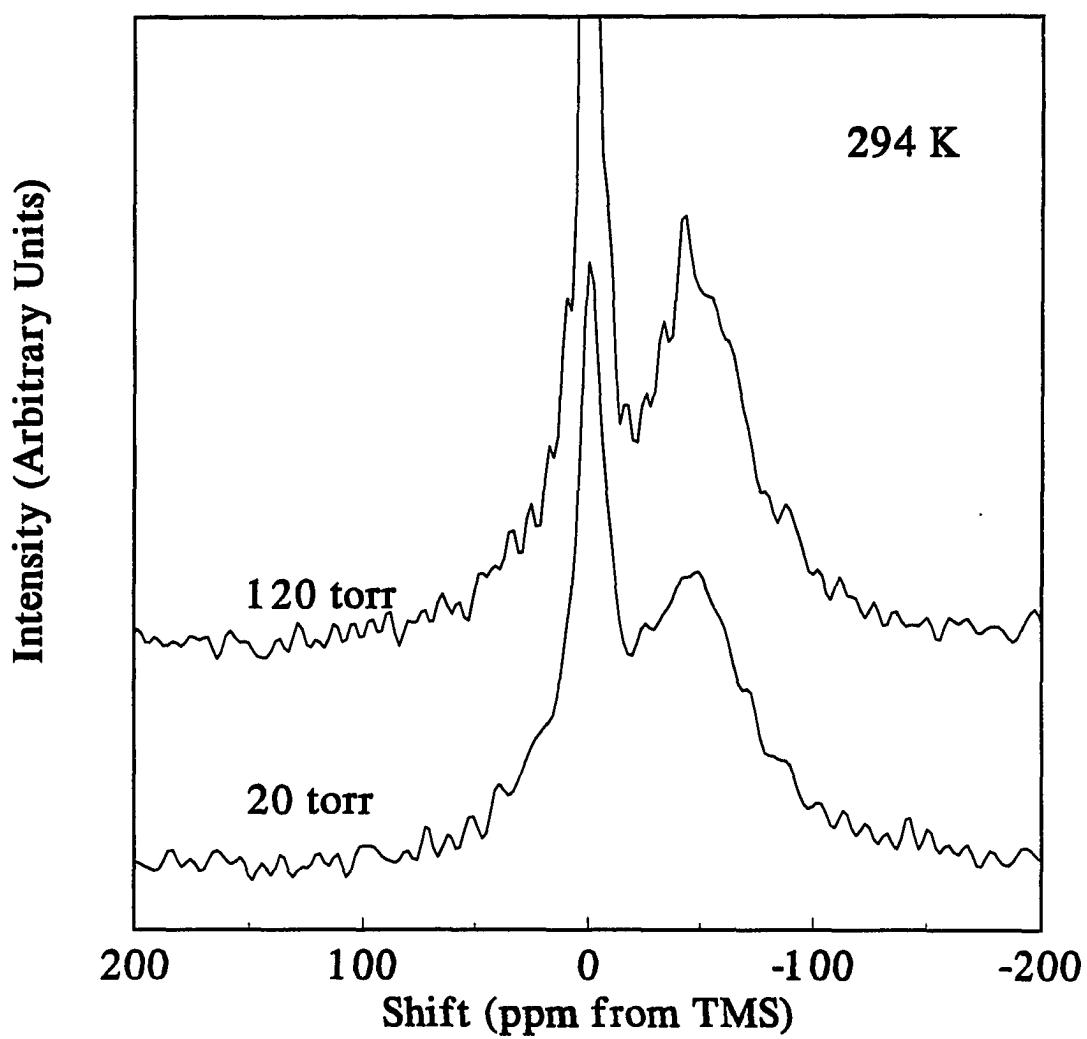
Figure 8. Effect of pressure on the hydrogen-on-metal resonance of Na/Ru/SiO$_2$, single excitation spectra
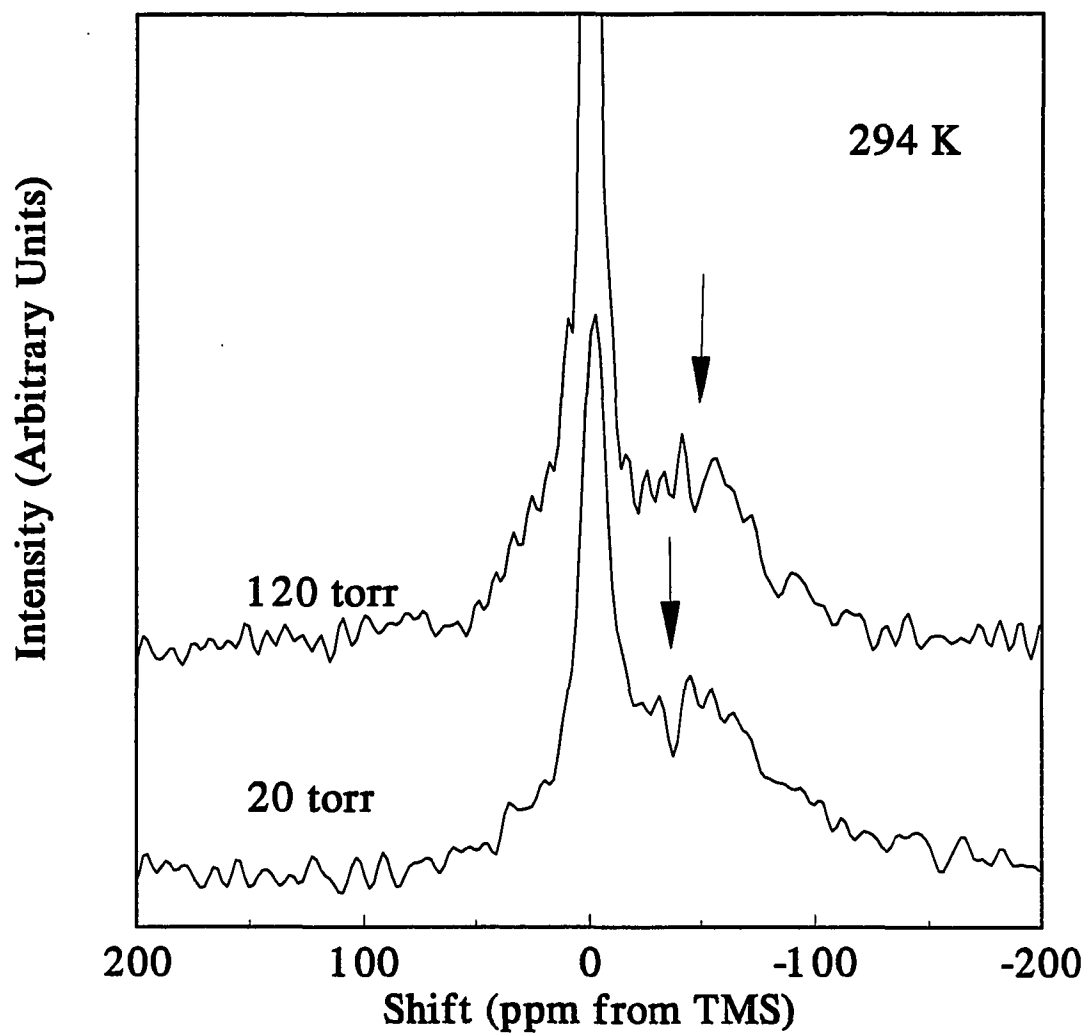
Figure 9. Effect of pressure on the hydrogen-on-metal resonance of Na/Ru/SiO$_2$, hydrogen-on-metal resonance was selectively inverted

DISCUSSION

Electronic Interactions Between the Na Promoter and the Ru Particles

The NMR spectra for a series of co-impregnated Na promoted catalysts are shown in Fig. 1. As can be seen, addition of Na did not influence the Knight shift of the adsorbed protons appreciably. The resonance frequencies obtained after deconvolution of the spectra by peakfitting were also uninfluenced from the presence of the Na promoter. This result is not surprising if one considers the fact that alkali promoters do not exist in their zerovalent state except under ultra high vacuum conditions. However, in the supported metal catalysts, alkali promoters usually exist in their oxide or hydroxide forms (8, 9). In their oxide or hydroxide state, alkali promoters can not donate electrons to the metal substrate as in the case of their zerovalent counterparts (10). Therefore, strong electronic interactions between the Na promoters and the chemisorbed hydrogen can not account for their role as a promoter for the Fischer Tropsch or the ammonia synthesis reaction.

Site Blocking Effects

Na promoters blocked the available hydrogen chemisorption sites on Ru irrespective of the preparation technique. The site blocking effects of Na promoters were monitored via ^1H NMR spectroscopy by spin counting. The results presented in Fig. 2 suggests that the site blocking effect of Na promoter was more significant for sequentially impregnated catalysts than for the co-impregnated

catalysts. We believe that, this effect is both due to the difference in the preparation chemistry as well as due to a decrease in the metal particle size. In fact, for K promoted Rh/SiO$_2$ catalysts, upon co-impregnation, smaller particle sizes were observed via X-ray diffraction techniques (4).

The promotional effects of Na and other alkali promoters may lie in their site blocking properties. The chain growth probability of a Fischer Tropsch synthesis catalyst, for example, depend very strongly on the hydrogenation capacity of the catalyst. In the presence of alkali promoters, the hydrogen chemisorption capacity of the catalyst decreases and the chain growth probability increases. In Fischer Tropsch synthesis, oxygen removal consumes hydrogen (forming water) on the unpromoted Co catalysts, whereas on promoted catalysts this takes place by carbon dioxide formation (i.e. carbon monoxide consumption) (11) which suggests that the hydrogenation capacity of the catalyst is hampered in the presence of alkali promoters.

Dynamics of Adsorbed Hydrogen

Alkali promoters not only influenced the availability of the chemisorbed hydrogen, but also the mobility as well. The highly mobile, weakly bound β state observed on an unpromoted catalyst was not present on the Na promoted Ru/SiO$_2$ catalysts (Fig. 4). The structure sensitivity of the β state was discussed by Bhatia et al. (18). For example, in the presence of Ag, the population of the β state was greatly diminished, suggesting the possibility that the presence of weakly bound β

state was correlated with the low coordinated edge and corner atoms. In the presence of Na promoters, the β state completely disappeared suggesting the possibility that the Na promoter preferentially occupied the low coordination sites.

To date, the decreased hydrogenation capacity of the Fischer Tropsch catalysts in the presence of alkali promoters was explained by the lessened availability of hydrogen. However, the diffusion coefficient measurements of hydrogen on sulfur covered Ru(001) single crystals indicated that (i) the hydrogen diffusion coefficient steadily decreased with increasing sulfur coverage and (ii) this decrease was not accompanied by a decrease in the activation energy for diffusion (20). Since sulfur and alkali promoters influence the hydrogenation ability of the catalysts in similar ways, a decrease in the hydrogen mobility in the presence of alkali promoters can also be expected.

This postulate could be tested by the selective saturation experiments done on the unpromoted and Na promoted catalysts. One can selectively excite part of an NMR resonance if the resonance is actually a superposition of a distribution of narrower resonances caused by a distribution of environments (heterogenous broadening). But when the chemical exchange is fast (with time constants shorter than the duration of the selective excitation pulses), the selective excitation process becomes ineffective (17). On unpromoted Ru/SiO$_2$ catalysts chemisorbed hydrogen experiences fast exchange at higher pressures, and the lines are homogeneously broadened (17). However, in the presence of Na promoters the NMR line due to the chemisorbed hydrogen were heterogeneously broadened as

indicated by the fact that the hydrogen-on-metal resonance could be selectively excited even at high pressures (200 torr) and at high temperatures (533 K). This result indicated that the two dimensional (surface diffusion) and/or three dimensional (adsorption/desorption) mobility of the chemisorbed hydrogen was significantly restricted in the presence of Na promoters even at high pressures and temperatures. This was also observed previously for the Cs promoted Ru/SiO_2 catalysts (19).

Interaction of Na Promoter with the Support

In addition to being deposited on the metal, Na promoters exchanged with the OH groups in the support as well. The proton density of the silica support decreased with Na loading for both sequentially and co-impregnated catalysts. The change in the number of OH groups as a function of alkali loading is given in Fig. 3. The decrease of OH proton intensity as a function of Na loading was more significant for the co-impregnated catalysts. Similar to the potassium promoted Ru/SiO_2 catalysts, this was probably due to a decrease in the metal particle size (1).

CONCLUSIONS

^{1}H NMR spectroscopy studies on Na promoted Ru/SiO$_2$ catalysts indicated that NA blocked hydrogen chemisorption sites on Ru but not on a one-to-one basis. There was no evidence for a through-the-metal electronic interaction between the chemisorbed hydrogen on the metal and the Na promoter. Na promoter also modified the support by exchanging with the protons of the hydroxyl groups. The weakly bound, structure sensitive β hydrogen population was not present on Na promoted catalysts, which suggested that Na could block electron deficient defect like sites. In the presence of Na promoters, the mobility of hydrogen on the Ru particles was significantly restricted.

ACKNOWLEDGEMENTS

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PAPER 4. CHARACTERIZATION OF SILICA AS A SUPPORT FOR Ru/SiO$_2$ CATALYSTS

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ABSTRACT

Silica support used in alkali promoted ruthenium catalysts was characterized via ^1H NMR spectroscopy. Pure silica treated with water via incipient wetness technique exhibited two distinct resonances with different spin lattice relaxation times. These groups exhibited different reactivity towards metal and alkali promoters during catalyst preparation. Alkali promoters had a significant affinity towards exchange with OH groups in the support. Their affinity increased with decreasing atomic size of the alkali metal, with Na being the highest. The effect of catalyst reduction temperature with and without ruthenium metal indicated that the total silanol group intensity decreased significantly with the reduction temperature over the range of 623-803 K. The presence of metals had an inhibiting effect on the silica dehydroxilation reaction. The number of protons in the silica support also decreased with the metal loading.

INTRODUCTION

The role of the catalyst support in the catalytic chemistry has long been overlooked. However, recent reports suggest that the support may play a more important role than just being the structural promoter (23-26). Recent experimental evidence (23 and the references therein) indicates the existence of a spilled over formate species on the alumina supported Ni, Pd and Pt catalysts. The methanation activity of this spilled over species is kinetically significant and is comparable to that from the metal surface itself. Similarly, theoretical calculations (24) suggests that methane formation from the spilled over CH_2O species and spilled over hydrogen on alumina is thermodynamically more favorable than the formation of corresponding alcohol. Kinetic studies of Fischer Tropsch synthesis on supported Co catalysts indicate a change in CO hydrogenation activity as a function of the catalyst activation method (25, 26): vacuum activated catalysts show a faster deactivation rate with a systematically higher turnover frequency (TOF) in comparison to air activated catalysts.

The interaction between a catalyst and a support depends largely on the nature of the metal and the support as well as the chemistry on the support surface during the catalyst preparation. Amorphous silica has a highly crosslinked polymeric structure with OH groups as the terminators. Due to the crosslinking in the bulk, fractal dimensionality arises in the microstructure. Fractal dimensions of about 2.2 have been reported for aerogels measured by ^{29}Si NMR techniques,

whereas densified silicas had a 3D structure (3). As any other material, surface atoms of silica is only partially saturated and therefore possess "residual valences". These residual valences are filled by OH groups bonded to the silicas creating silanol groups on the surface (4, 6) which can be classified into three main groups: Isolated silanols, geminal silanols and siloxanes.

i) Isolated silanols, $Si(O_{0.5})_3OH$[1]: These OH groups belong to a silicon atom which is bound to three other silicon atoms via an oxygen atom. Isolated silanols may form hydrogen bonding with the oxygen of the neighboring OH group forming "vicinal" hydrogen populations.

ii) Geminal silanols, $Si(O_{0.5})_2(OH)_2$: This species have two OH groups attached to a two coordinated silicon atom.

iii) Siloxanes, $(SiO_{0.5})_4$: Siloxanes form the bulk of the material and possess no OH groups.

Since the interaction of the adsorbates with the silica takes place via a reaction with the surface silanol groups, the chemistry of the surface depends significantly on the nature of the different hydroxyl groups. For example, the size distribution of Ni particles on silica is strongly influenced by the characteristic silica ring structure. Silicas with a high content of 3 membered rings in their structure was reported to produce a bimodal nickel particle size distribution (8). Furthermore, the interaction of metals and metal salts with the OH groups on the

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[1] Partial stoichiometry on oxygen atom indicates that oxygen is bound to two silicon atoms.

silica surface during catalyst preparation depends on several factors such as the acidity of the environment, the affinity of the metal towards interaction with the OH groups, and the presence of other cations in solution (1, 4). The importance of the acidity of the solution during catalyst preparation has long been recognized. Silica surface has its isoelectronic point at around pH=1.0-2.0. At higher values of pH, the surface is negatively charged, therefore silica surface can adsorb and react with cations effectively (4, 9). As the pH of the solution increases, on the other hand, silica dissolves in the form of silicic acid, $Si(OH)_4$. This support dissolution was reported to decrease the final BET surface area of the support (9).

The relative affinity of the metals towards interaction with support surface also plays an important role on how well the metals could be dispersed on silica. The dispersion capacity of metal oxides on the supports depend on the surface structure of the support and on the valance type of the metal or metal oxide (17). For example, Mo could be better dispersed on silica than W which can be explained by the fact that the extent of the chemical reaction via condensation of OH groups of silica and molybdate ions is much higher than between tungsten and silica (7). Finally, in multicomponent systems where more than one species are involved, the bulk mixing properties of these species and their relative interaction with the support play an important role in determining how each of these species interact with each other. For example, the metals or oxides which do not mix in bulk tend to interact with the support surface independently and form individual clusters.

High resolution ^{1}H and ^{29}Si NMR spectroscopy has been extensively used to characterize the structure of silicas (2, 5, 6, 14, 15, 16, 21). In the present paper, results on the characterization of the different hydroxyl sites on a Cab-O-Sil HS5 silica in the presence of ruthenium metal and alkali promoters via ^{1}H NMR spectroscopy will be reported. The relative reactivity of these OH groups with ruthenium and alkali promoters will be discussed.

METHODS

Cab-O-Sil HS5 with a specific surface area of 300 m^2/g was used as the catalyst support. Three series of alkali promoted Ru/SiO$_2$ catalysts were prepared with sodium, potassium and cesium. Incipient wetness technique was used for catalyst preparation. Alkali promoters were incorporated in the catalyst via a sequential impregnation technique. The details of the catalyst preparation, NMR sample preparation and the NMR experiments were given elsewhere (11, 12). In addition to the catalyst samples, a pure support sample was prepared by impregnating Cab-O-Sil with distilled water via an incipient wetness technique.

NMR experiments were carried out in a home built spectrometer with a proton (^{1}H) resonance frequency of 220 MHz. All the measurements were done at room temperature. Spin lattice relaxation times were measured by an inversion recovery pulse sequence (π-τ-π/2). The absolute intensities of NMR peaks were obtained by comparing the signal intensity with a water reference sample of known spin count. The water sample was sealed in a capillary tube of the length of the catalyst samples to account for the inhomogeneities in the pulse lengths along the probe coil (13). All NMR measurements were done at 294±1 K.

RESULTS

^{1}H NMR Spectroscopic Characterization of Pure Silica

Single $\pi/2$ excitation ^{1}H NMR spectrum of a silica sample treated with water via the incipient wetness technique, reduced and evacuated under the same conditions as the catalyst samples exhibited a single resonance centered around 3 ppm downfield from TMS with a full width at half maximum (FWHM) of approximately 15 ppm (2.6 kHz) (Fig. 1). Spin lattice relaxation time of this sample measured via the inversion recovery technique (π-τ-$\pi/2$) could be best represented with a double exponential decay with T1's of 1 and 4.5 s, respectively (Fig. 2). At a delay time, τ, of 2 s, the spectrum clearly exhibited two distinct features (Fig. 3): a broad feature of approximately 50 ppm (10 kHz) FWHM and a sharp resonance with a linewidth of approximately 12 ppm.

Effect of Reduction Temperature

To observe the effect of reduction temperature on silanol protons two series of NMR samples were prepared. The first series was prepared from water treated silica and the second series was prepared from a 4 wt% Ru/SiO$_2$. The samples were reduced in static hydrogen for two hours. Every 30 min. hydrogen was evacuated and replenished. The reduced samples were evacuated at 573 K for 4 hours. After evacuation the samples were dosed with hydrogen at 100 torr, allowed to equilibrate for 1 hour and evacuated to 10^{-5} torr for 5 min such that only strongly bound hydrogen (13) remained on the catalyst surface.
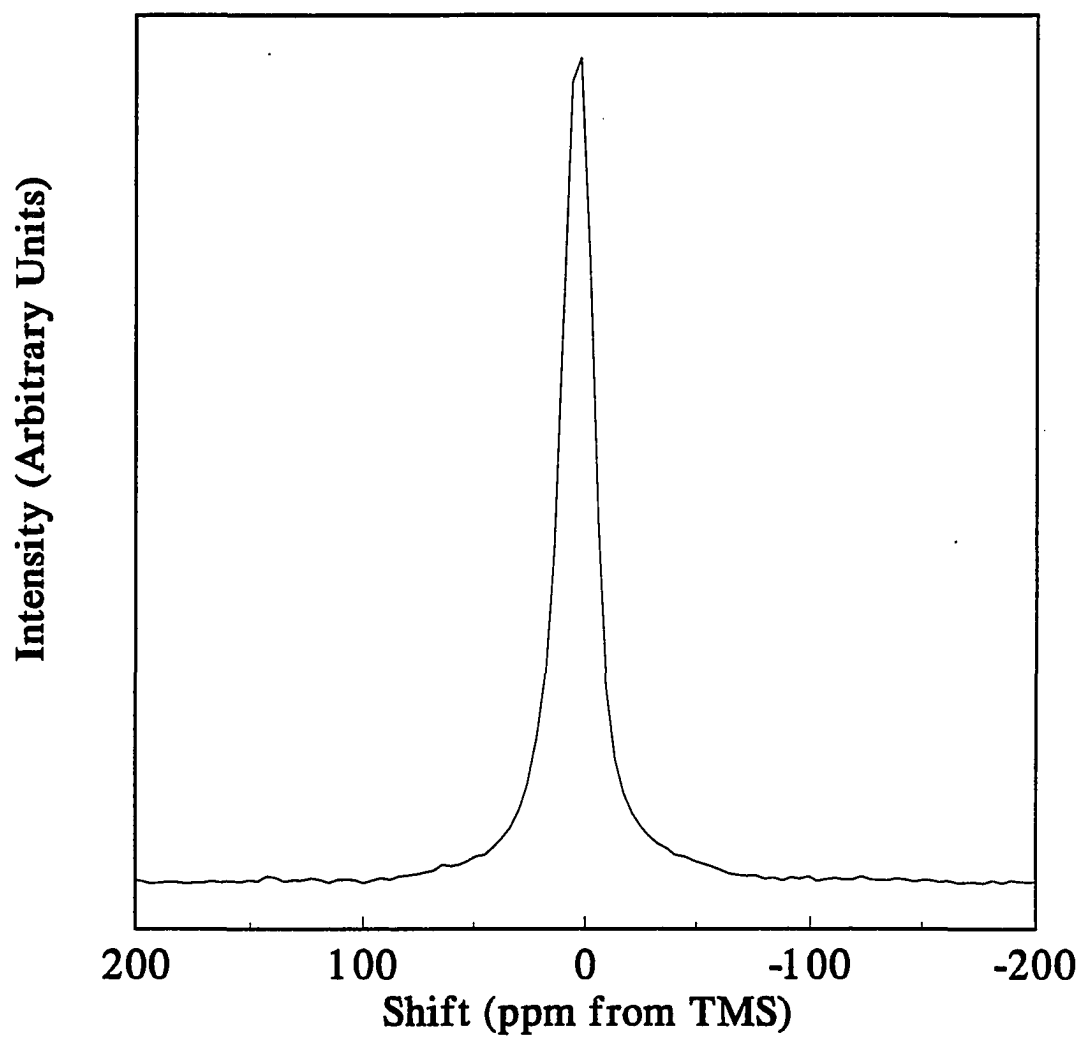
Figure 1. Single excitation NMR spectrum for a dehydrated, reduced and
evacuated silica sample
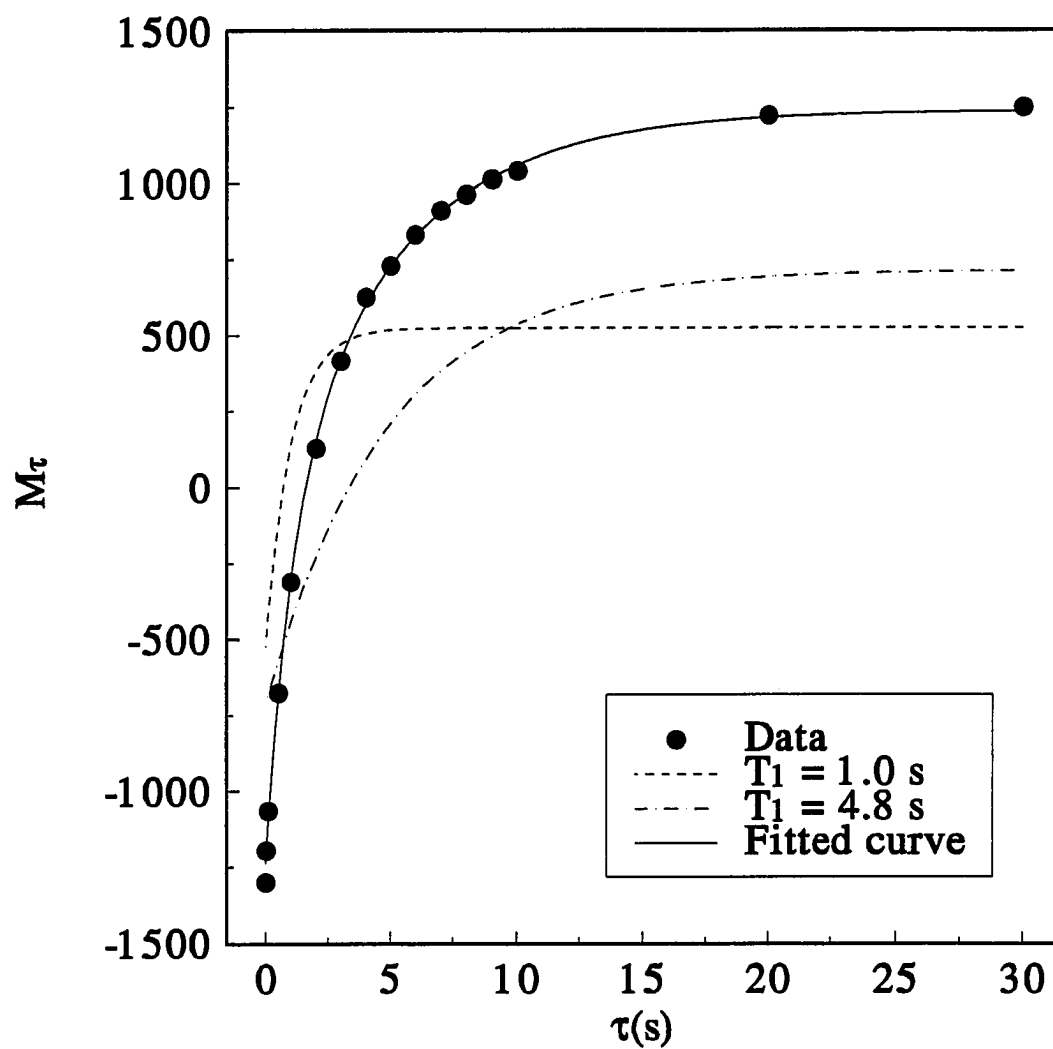
Figure 2. Inversion recovery data of reduced and evacuated silica sample
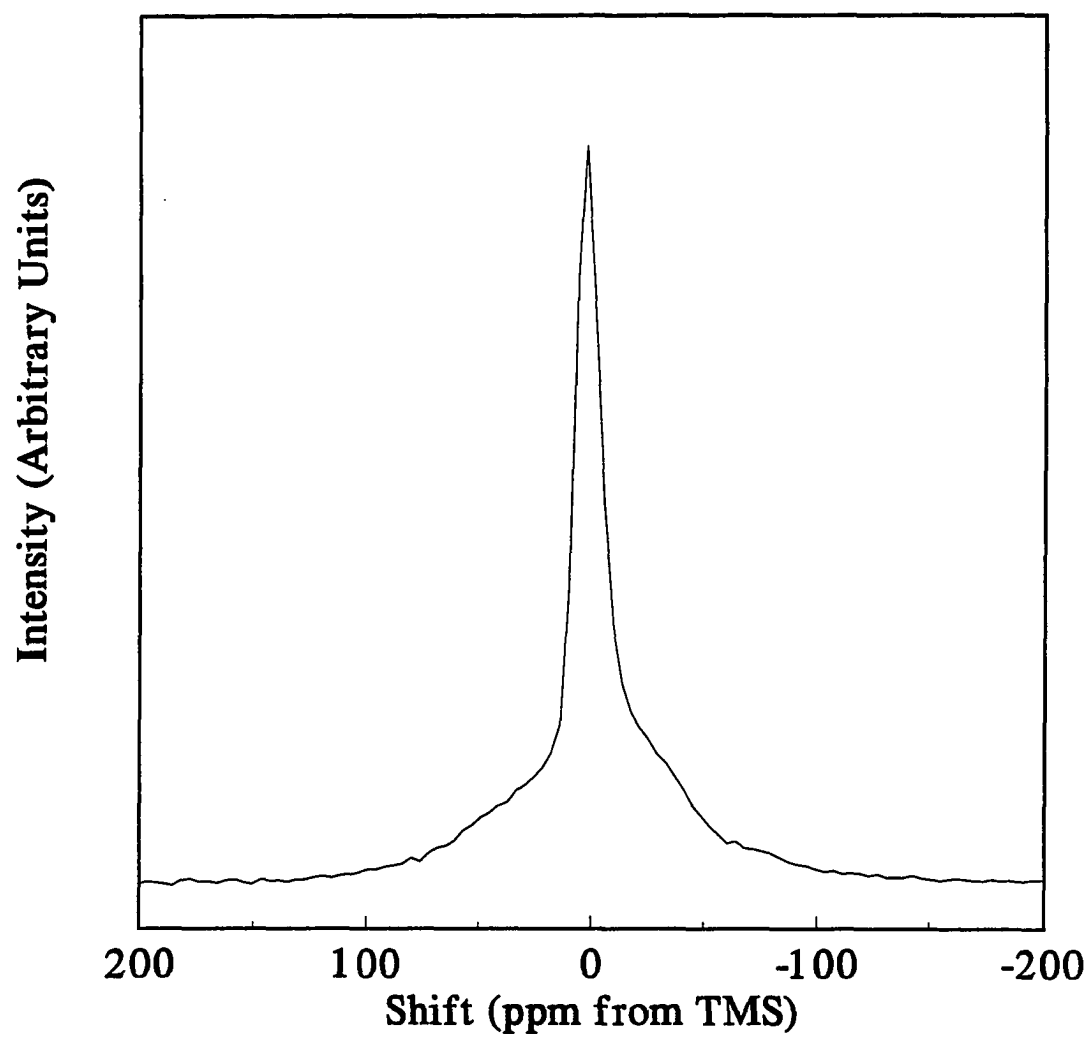
Figure 3. The NMR spectrum of pure silica under the inversion recovery pulse
sequence after a delay time τ=2 s

Quantitative analysis of the silanol protons via NMR spectroscopy is shown in Fig. 4. The silanol intensity decreased as a function of reduction temperature for both sample series. The decrease in silanol proton intensity as a function of reduction temperature was smaller for the samples with Ru. The change in the linewidths of the spectra with the reduction temperature was not significant.

To monitor whether any change in the particle size has occurred, the metal dispersions were measured using NMR spectroscopy by spin counting the strongly bound hydrogen on the metal. As seen in Fig. 5, the number of hydrogen chemisorption sites on ruthenium did not change very much with the reduction temperature, however, the NMR Knight shifts (Fig. 6) changed slightly in the direction of increased particle size (13).

Effect of Metal Loading

To investigate the role of the metal loading on the OH groups in the silica, a series of catalysts were prepared with different metal loadings via the incipient wetness technique. These catalysts were reduced and evacuated for 4 hours at 723 K and overnight at room temperature. One hundred torr of hydrogen was dosed on these samples at room temperature. After 10 min, the samples were evacuated for 5 min. to a pressure of 10^{-5} torr and sealed. The NMR spectra were acquired by accumulating 30 scans. A repetition time of 50 seconds was used between each to restore full equilibrium magnetization.
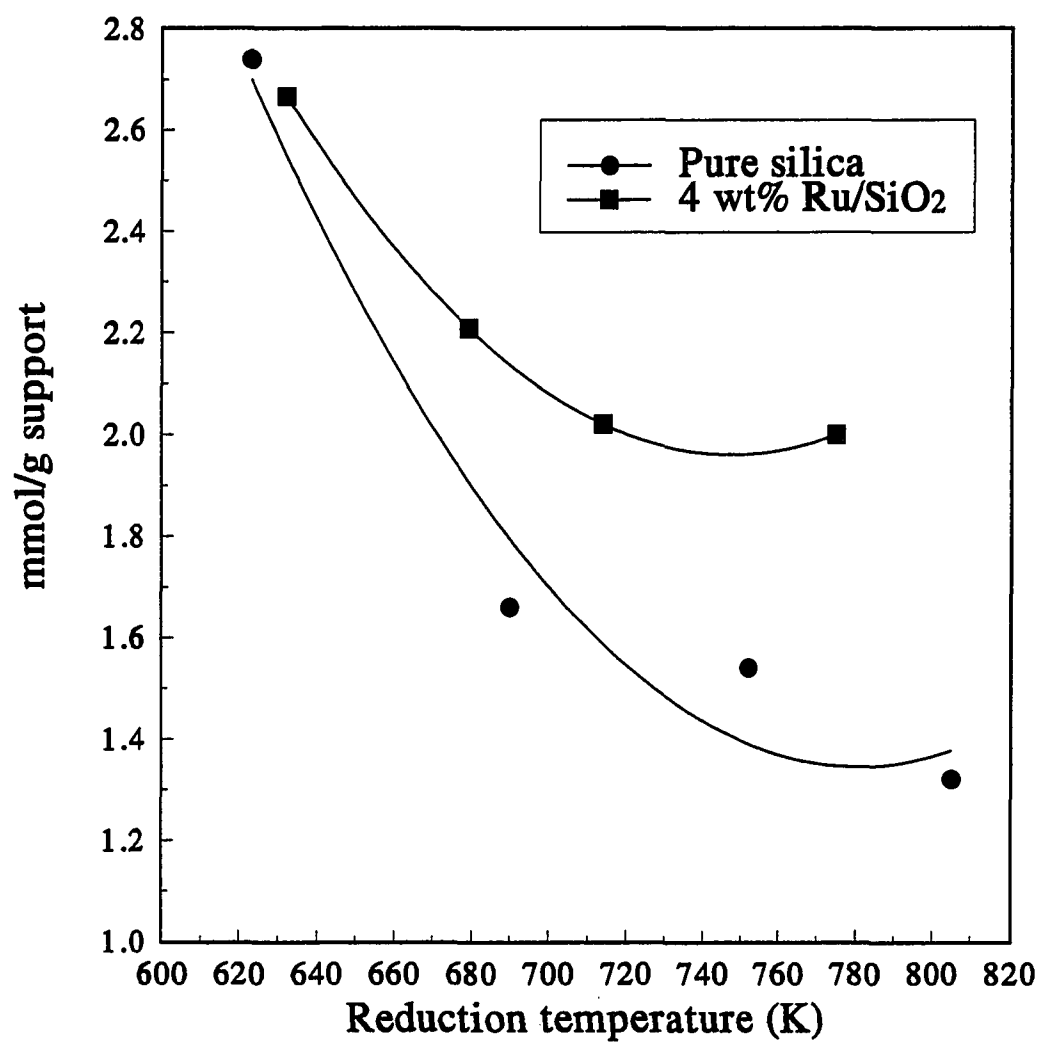
Figure 4. Effect of the reduction temperature on the silanol proton intensities
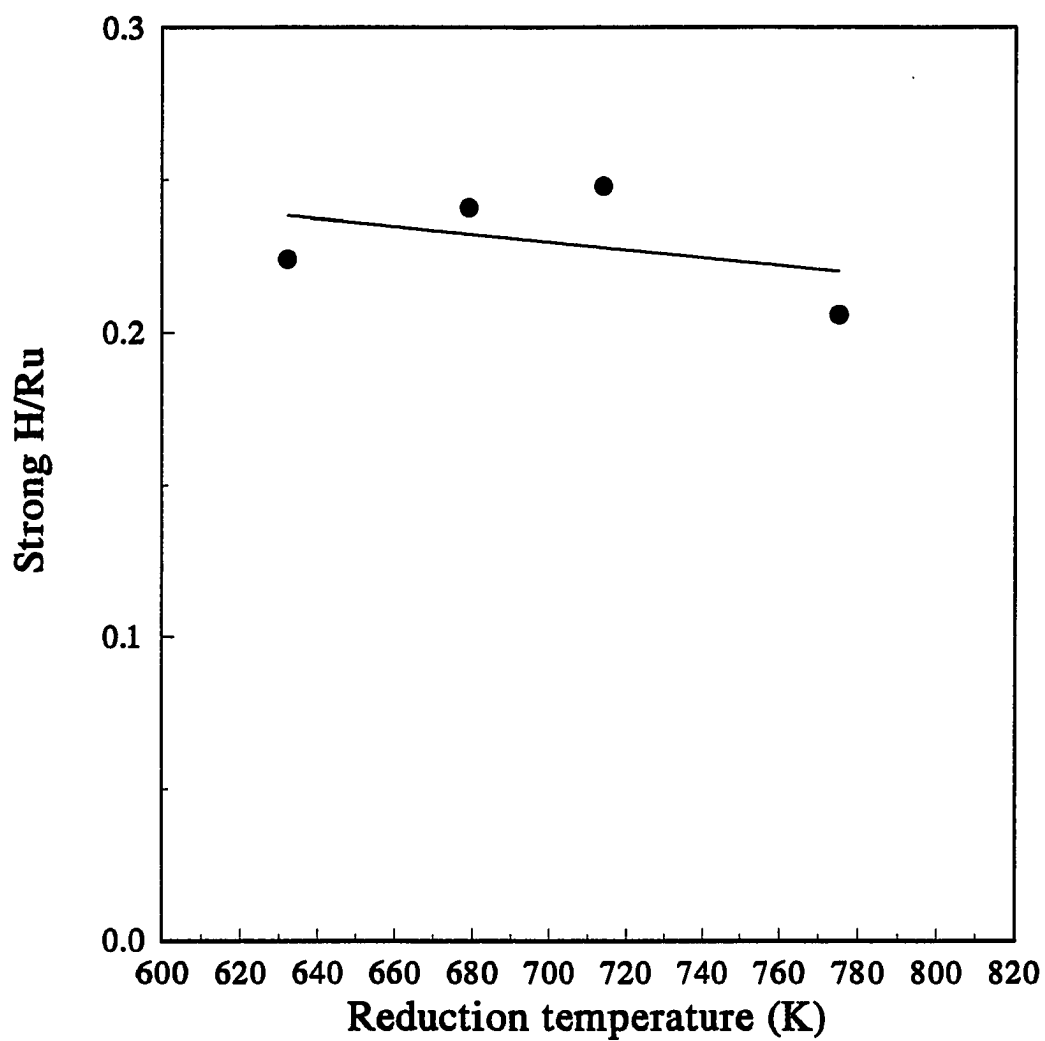
Figure 5. Effect of the reduction temperature on metal particle dispersion measured by strong hydrogen chemisorption
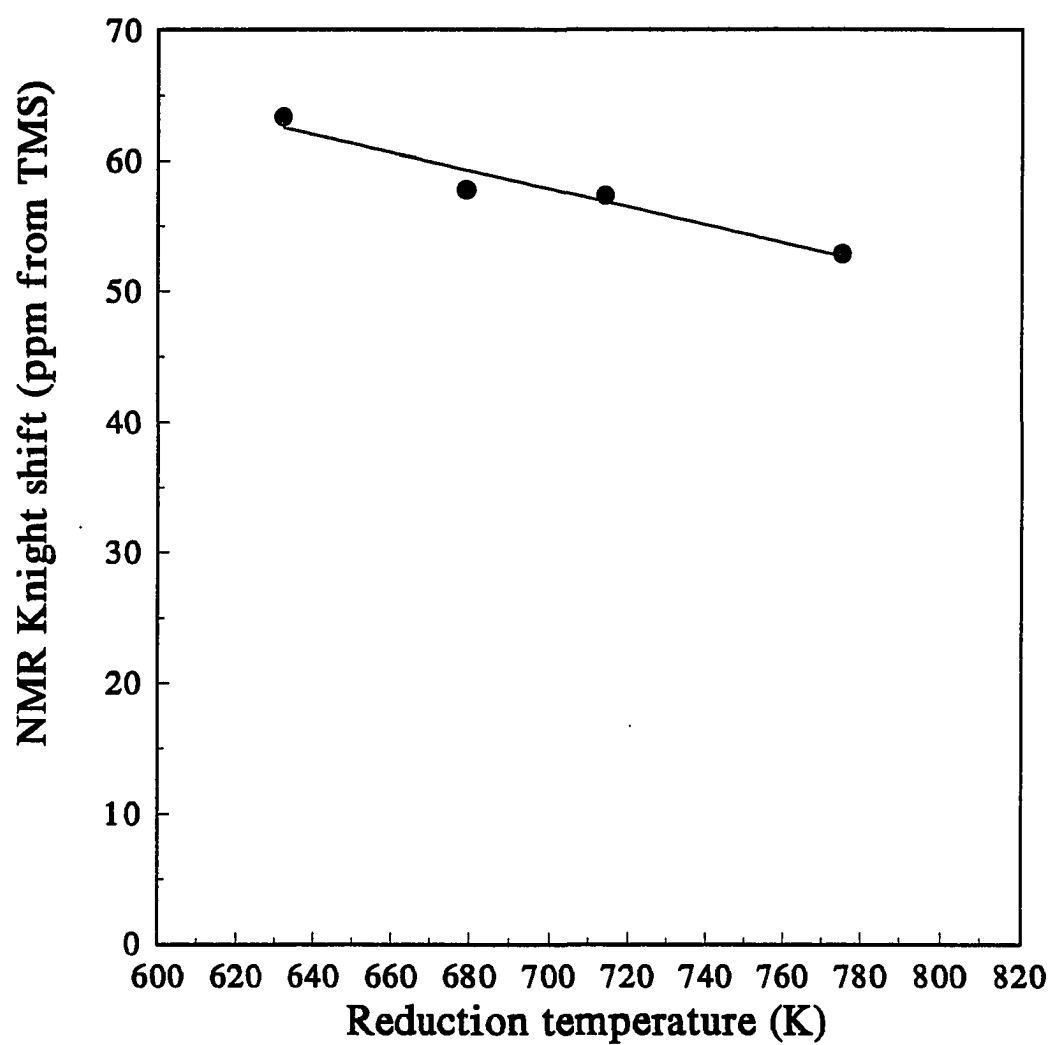
Figure 6. Effect of reduction temperature on the NMR Knight shift

The spectra were normalized with respect to the amount of the support. The integrated intensity of the NMR spectra of the catalysts indicated a linear decrease in the intensity due to the OH groups in the silica support as a function of metal loading (Fig. 7). However, the fractional intensity decrease with the metal loading was not on a one-to-one basis.

Effect of Alkali Promoters

Three series of alkali promoted catalysts were prepared via a sequential impregnation technique. Na and K promoted catalysts were prepared from a catalyst with a Ru loading of 4 wt%, Cs promoted catalysts had a Ru metal loading of 10 wt%. In addition to the promoted catalysts, each series of catalysts contained a sample prepared from an alkali promoter supported on the silica support without any Ru. All of the alkali metals showed an affinity towards exchange with the protons of OH groups on the support surface. The OH group intensity systematically decreased with the alkali loading. The intensity of the silanol protons were normalized with respect to the OH group intensity of the unpromoted catalyst and plotted against alkali loading in Fig. 8.

The spin lattice relaxation times, T1, of the OH groups were also influenced in the presence of the alkali promoters. The T1 of Na and K promoted series of catalysts were obtained by the inversion recovery technique. The T1's are given in Tables 1 and 2 for Na and K promoted catalysts, respectively.
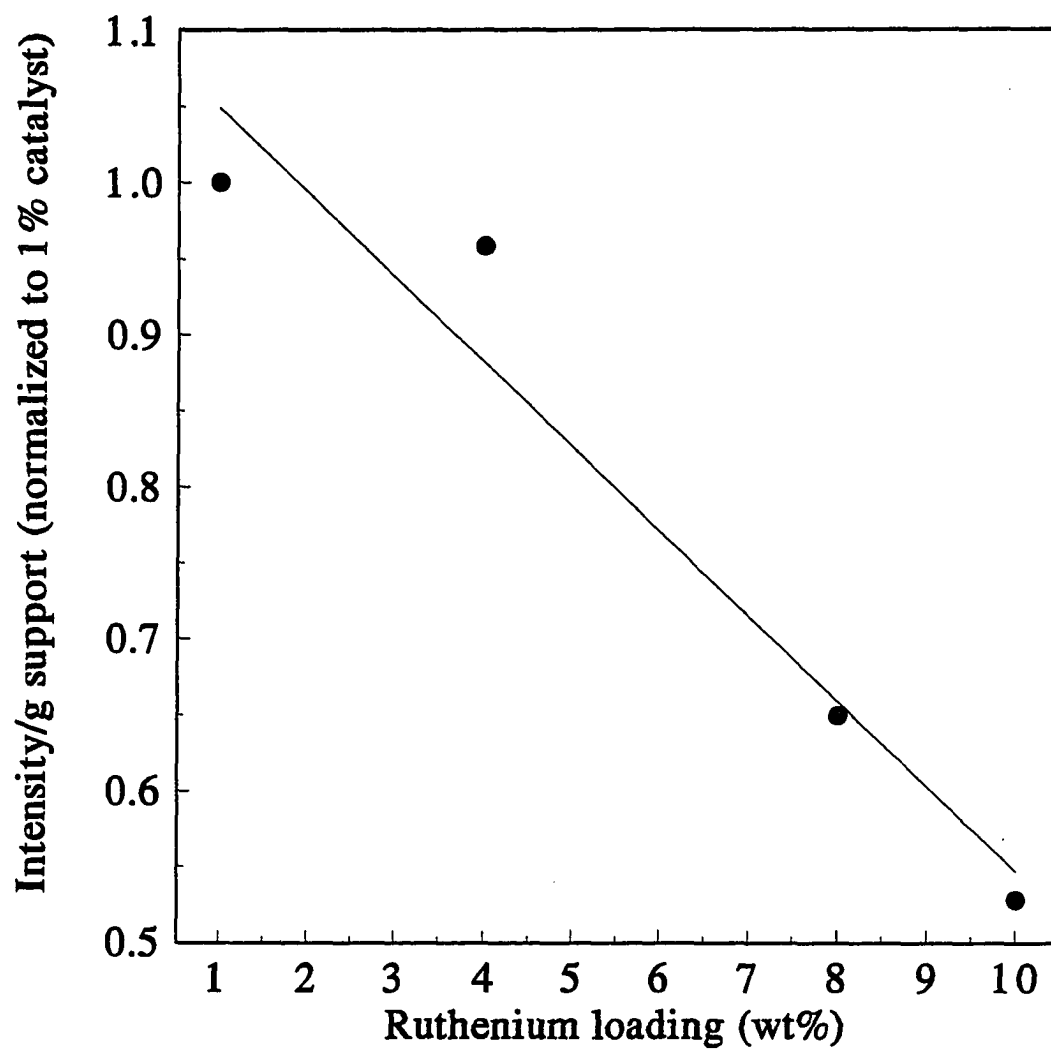
Figure 7. Effect of the metal loading on the silanol proton intensities
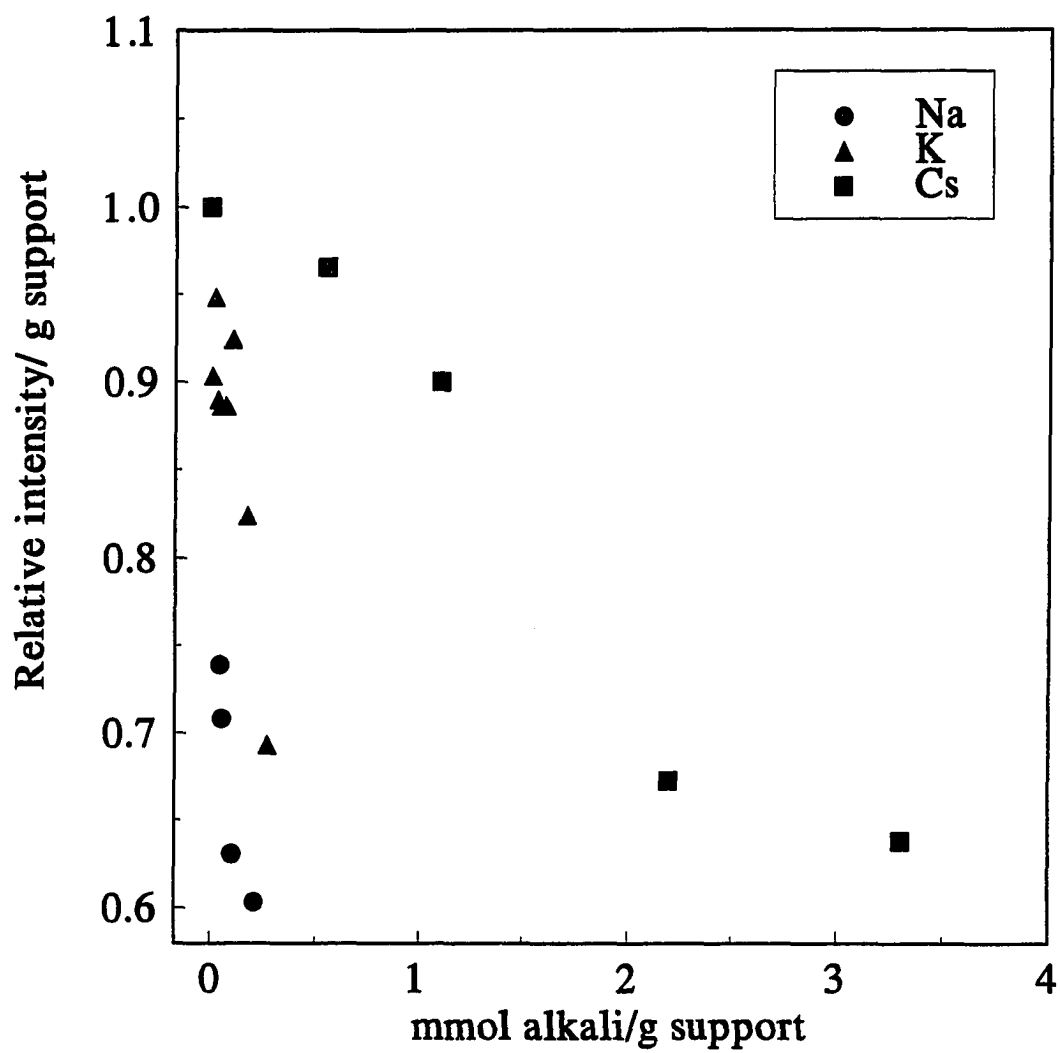
Figure 8. Effect of alkali loading on the silanol proton intensity

Table 1. The spin lattice relaxation times of two types of OH groups on the silica surface as a function of Na loading for the sequentially impregnated series

Atomic % sodium	T1 of fast relaxing species (s) Error margins are ±50 ms	T1 of slow relaxing species (s)
0	0.4	3.8
1	0.28	4.6
3	0.15	4.3
7	0.16	4.7
10	0.2	3.8
12	0.11	3.4
16	0.14	3.1
20	0.23	3.1
100	N/A	17.2

Table 2. The spin lattice relaxation times of two types of OH groups on the silica surface as a function of K loading for the sequentially impregnated series

Atomic % potassium	T1 of fast relaxing species (s) Error margins are ±50 ms	T1 of slow relaxing species (s)
0	1.4	7
2	2.9	10
10	3.6	13
15	4.3	11.6
20	4.6	7.8
40	2.5	5.3
100	N/A	24.1

DISCUSSION

The metal dispersions of the supported catalysts depend very strongly on the extent of interaction of the metals or oxides with the support surface during the catalyst preparation. The chemistry of the metal or metal oxides with the surfaces of the oxide supports is not very well understood due to the complexity of these materials and the lack of proper experimental techniques that enable the investigation of the surfaces of the amorphous materials. ^{1}H NMR spectroscopy enabled us to investigate the interaction of the hydroxyl groups on the silica surface with ruthenium metal and various alkali promoters at several different levels of metal and promoter loadings and under different pretreatment temperatures.

The single excitation ^{1}H NMR spectrum of a reduced and evacuated silica sample exhibited only a single resonance centered approximately 3 ppm downfield of TMS with a linewidth of approximately 12 ppm (3 kHz) (Fig. 1). However, inversion recovery data of the same sample indicated the existence of at least two different proton environments with different relaxation constants (1 s and 4.5 s) (Fig. 2). The NMR spectrum of the sample excited with an inversion recovery pulse sequence with a delay time of 2 s shown in Fig. 3 provided the supporting spectroscopic evidence for the existence of at least two different proton populations in the pure silica sample. After a delay time of two seconds, two resonances with linewidths of ~15 ppm and ~50 ppm were distinguishable.

The presence of these proton populations were noticed previously by using MAS ^{1}H NMR spectroscopy (7, 14). However, their assignments are still controversial. For example, the broad component of the spectrum was observed as spinning sidebands in the magic angle spinning (MAS) ^{1}H NMR spectrum and was attributed to the proton pairs highly coupled to each other (14). The problem, whether these proton pairs are the geminal silanols or coupled isolated silanols, has yet to be solved.

The CP-MAS ^{29}Si NMR investigations of the aerosil silica (5, 14) with different proton densities indicated the existence of geminal silanol groups (Si(OH)$_2$) even after thermal evacuation of the samples at 1273 K. A CP-MAS ^{29}Si NMR investigation on amorphous silicas at various degrees of hydration showed that the ratio of Si(OH)$_2$ to Si(OH) groups was constant (1 to 4) which indicated an equilibrium in the distribution of the hydroxyl groups on the silica surface. The single excitation broadline ^{1}H NMR studies carried out in this work could not provide a strong evidence regarding the distribution of protons among various possible OH groups that could exist on the support surface.

The effect of the reduction temperature did not influence the metal particle size as observed by the proton spin counting of the hydrogen on the metal resonance (Fig. 5). However, the silanol intensity decreased significantly with the reduction temperature. The same effect was observed with a pure silica sample in the absence of the metal. The decrease in the number of protons per gram of support was higher for the pure support. Since the contribution of the spilled over

hydrogen in the presence of metals on the intensity of the 3 ppm resonance is within 1% of the total intensity of the resonance (12), the larger number of OH protons in the Ru/SiO_2 sample was attributed to a local dilution effect such that the condensation of adjacent OH groups close to the metal particles were inhibited.

The total OH group intensity was also dependent on the metal loading. The results presented in Fig. 7 indicated that the number of the OH protons decreased with an increase in the metal loading. However, the fractional change was not on a one to one basis. A similar effect has been observed in the silica supported Mo and W catalysts (7). The decrease in the OH groups with the metal loading was higher for Mo than for W. Mo could be better dispersed on silica than W, which was explained by the fact that the extent of the chemical reaction via condensation of OH groups of silica and molybdate ions was much higher than between tungsten and silica (7). The change in the intensity of the 3 ppm resonance was not accompanied by a change in the linewidth (approximately 12 ppm for all loadings) which indicated that the local environment of the OH groups were not significantly influenced in the presence of the Ru metal. If the line broadening was due to the dipolar coupling of the protons, an increase in the average proton-proton distance had to result in a decrease in the FWHM of the 3 ppm resonance. The absence of a change in the linewidth of the 3 ppm resonance indicated that metals existed on certain patches of the support surface such that the local proton density of the rest of the support surface was not influenced.

The number of protons in the support was also influenced in the presence of the alkali promoters. The relative change in the OH group intensity as a function of alkali loading was plotted in Fig. 8. The intensities of the 3 ppm resonances were normalized with respect to that of the unpromoted catalyst. The relative loss of OH intensity with respect to the alkali loading decreased in the increasing atomic number.

The position of the equilibrium

$$(-OH)_n + M^{n+} = M(-O)_n + nH \tag{1}$$

depends on the basicity of the framework and its affinity towards metal ion in question. In general, cation exchange equilibria are controlled by two mechanisms (10):

a) coulombic interactions between the counter ions and the fixed groups of exchanger;

b) ion-dipole and ion induced dipole interactions between the counter ions and water molecules (ionic hydration).

When coulombic interactions are weaker than the ion dipole interactions, a "normal" affinity sequence is observed. That is, the ion with larger hydrated radius tends to become displaced by the ion of smaller hydrated radius. For alkali metals, this sequence goes as $Cs^+ > K^+ > Na^+ > Li^+$. When the coulombic interactions predominate over the ion-dipole interactions, the selectivity becomes reversed ($Li^+ > Na^+ > K^+ > Cs^+$). In the present situation, the data suggest that the affinity of

alkali metals increase in the sequence ($Na^+>K^+>Cs^+$), i.e., coulombic interactions dominate over the ion dipole interactions. However, it has to be noted here that (i) part of the alkali in solution was deposited on the metal surface and (ii) the silica support was modified in the presence of the metal.

In the presence of alkali promoters, in addition to the intensity changes, the T1 and the linewidth of the OH group resonance was also influenced. The linewidth of the resonance systematically decreased with the alkali loading (12 ppm for unpromoted catalyst, 4.5 ppm for a Cs:Ru=3 10 wt% Ru/SiO_2 catalyst). The decrease in the linewidth of the OH resonance with alkali loading indicated that the average proton distance increased in the presence of alkali promoted systems.

T1 of the OH groups in the samples doped with pure alkali promoter showed a systematic increase with the atomic size of the dopant (Cs~2 min; K~24s; Na~17 s; pure silica~5 s). Since the mechanism for the spin lattice relaxation of the OH protons is not very well understood, any comment would be highly speculative. As can be seen from Tables 3.1 and 3.2, the T1 of OH protons with a longer relaxation time went through a maximum with the alkali loading. Since the number of silanol protons decrease with alkali loading, the increase in T1 with alkali loading can be due to a simple dilution effect. The complicated nature of T1 relaxation processes makes it difficult to have a simple explanation for the reversal of the dilution phenomena after a certain alkali loading. Possible reasons for this phenomenon include (i) a change in the chemical nature of alkali species; (ii) a

clustering effect or (iii) a creation of relaxation centers at higher loadings of alkali. One should also note that the spin lattice relaxation times of the OH groups are significantly higher for the silica samples doped with alkali promoters only. Therefore the maxima observed in the presence of the metals can be due to the changes induced in the support in the presence of spilled over hydrogen. The comparison of the T1's of the OH groups of the alkali doped silica surfaces with (4-7 s) and without (15 s-2 min) the metal suggests that in the presence of the metal, the interaction of the OH protons with the surrounding thermal lattice was more efficient and the alkali doped silica surface is not representative of the silica surface when alkali promoters and the metals coexist.

The present results suggest that the support surface is significantly modified in the presence of metals and/or promoters. It is widely accepted that the acidity of the support materials depend on the number and nature of the OH groups. In the presence of metal particles, the support acidity is reported to be modified due to the changes in the number of the OH groups on the support surface and the structural changes such as modified O-H bond angles and lengths (18, 19, 27). When the dispersion of a catalytic material was adjusted by changing the metal loading, the support surface is also modified. Johnson *et al.* (26) made the observation that the "chemical nature of the support surface appears to be the controlling factor in determining specific activity of supported Co catalysts". These results suggest that it is imperative to characterize the support and the metal

surfaces simultaneously when the structure sensitivity of the catalytic reaction was

under investigation.

CONCLUSIONS

The silica support was characterized in the presence of Ru metal and Na, K and Cs promoters. The total number of OH groups decreased with both Ru loading and alkali loading. The exchange efficiency decreased in the order Na>K>Cs. Increasing reduction temperatures did not influence the number of the strongly bound hydrogen chemisorption sites on the metal, however, a significant decrease was observed in the total number of the OH groups with the reduction temperature.

ACKNOWLEDGEMENTS

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PAPER 5. OPTIMIZATION OF VOLUMETRIC HYDROGEN CHEMISORPTION AS A CHARACTERIZATION TECHNIQUE FOR Ru/SiO$_2$ CATALYSTS

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ABSTRACT

Direct ^{1}H NMR evidence was obtained for an irreversibly bound component of spilled over hydrogen which caused a large discrepancy between the dispersion values measured by ^{1}H NMR and volumetric techniques. The discrepancy was larger for longer hydrogen exposure times. Based on *in-situ* ^{1}H NMR evidence, optimum conditions for the volumetric chemisorption were determined to minimize the amounts of the irreversibly bound spilled over hydrogen. The values of the strongly bound hydrogen on ruthenium obtained from the modified volumetric chemisorption measurements agreed very well with the results of the ^{1}H NMR spin counting.

INTRODUCTION

Hydrogen chemisorption is a widely used method to characterize the metal catalyst surfaces (1, 2). The relatively simpler nature of hydrogen adsorption and generally accepted 1:1 stoichiometry on most metals makes it the most feasible adsorbate for surface characterization of supported ruthenium catalysts. However, the volumetric chemisorption measurements involve inaccuracies due to the presence of an irreversibly bound spilled over hydrogen (3, 4). The amount of the irreversibly bound spilled over hydrogen is a strong function of the metal, the support, the metal dispersion, the adsorption temperatures and the hydrogen exposure times (3-7, 12-13).

The volumetric hydrogen chemisorption technique currently used to characterize the supported metal catalysts was described in detail in the articles by Dalla Beta (1) and Goodwin (2). The volumetric hydrogen chemisorption technique allows one to measure the strongly bound hydrogen amounts, which was postulated to have 1-to-1 stoichiometry with the surface metal atoms. In the standard chemisorption technique, room temperature isotherms are obtained for the total and weakly bound hydrogen over a pressure range of 0-100 torr. In this pressure range, both the total and the weak hydrogen adsorption isotherms show a linear dependency on pressure. The strongly bound hydrogen amounts can be obtained by extrapolating the adsorption isotherms to zero pressure and taking the difference between the intercepts of the total and weakly bound hydrogen

isotherms. This technique does not overlook the possibility of the presence of the spilled over hydrogen. However, it involves an assumption that the spilled over hydrogen is weakly bound at room temperatures and it can be eliminated by evacuating at 10^{-5} torr for 10 min.

In this paper, we will report a direct ^1H NMR evidence for an irreversibly bound spilled over hydrogen on the silica support which interferes with the surface characterizations of supported metal catalysts. We will also report optimum conditions for the volumetric chemisorption experiments such that the influences from the strongly bound spilled over hydrogen are minimized.

METHODS

Catalyst Preparation

All of the catalysts used in this work was prepared via an incipient wetness technique using a ruthenium nitrosyl nitrate (26% Ru, Johnson-Matthey) salt or a ruthenium nitrosyl nitrate solution (Strem Chemicals, 1.5 wt% Ru) as precursors. A 4 wt% catalyst was prepared from the ruthenium nitrosyl nitrate salt obtained from Johnson-Matthey by dissolving appropriate amount of salt in 2.2 ml water/g support. A slurry was prepared by impregnating the support (Cab-O-Sil HS5) with this solution. The slurry was dried in air at 383 K for 8 hours. The final catalyst had a dispersion of approximately 10% measured by ^{1}H NMR spectroscopy. This catalyst will be designated as Ru/SiO$_2$(I). A second catalyst was prepared from ruthenium nitrosyl nitrate solution obtained from Strem chemicals. The volume of the solution needed to prepare a 4 wt% Ru/SiO$_2$ catalyst was 2.6 ml/g support. After the slurry was prepared, this catalyst was dried in air overnight and at 383 K for 2 hours. The final catalyst had a dispersion of approximately 20% measured by ^{1}H NMR spectroscopy. This catalyst will be designated as Ru/SiO$_2$(II). A third catalyst was prepared by the same method as Ru/SiO$_2$(I) at a Ru loading of 10%. This catalyst will be called as Ru/SiO$_2$(III).

Volumetric Chemisorption

Volumetric hydrogen chemisorption measurements were done by using a home built adsorption apparatus, described elsewhere (8). About 1 gram of catalyst was placed in a Pyrex cell with a coarse frit which would enable the flow through reduction of the catalyst. The catalyst was heated up to 423 K under helium flow which was maintained in the cell for about 30 min. to remove as much moisture as possible before reduction started. Then H_2 was allowed in the chamber and the catalyst was heated up to 623-723 K at a heating rate of 6 K/min. After the desirable reduction temperature was reached, reduction was carried out for 2 hours. The reduction was followed by evacuation to remove the traces of adsorbed hydrogen. Hydrogen chemisorption experiments were carried out at temperatures between 293-393 K. Hydrogen exposure times were varied between 10 minutes to several hours. The total hydrogen adsorption isotherm was measured in the pressure range of 0-100 torr. The reversible hydrogen adsorption isotherm data were collected in the same range after an evacuation to 10^{-5} torr following the total adsorption.

NMR Experiments

The *in situ* NMR experiments were carried out in a home built spectrometer operating at 250 MHz ^1H resonance frequency and a home built probe which could operate between 100 and 800 K. About 100 mg of unreduced catalyst was placed in the sample chamber of the in-situ probe which was connected to the glass

manifold. The sample pre-treatment procedure for the *in situ* experiments was similar to that of volumetric chemisorption measurements. After the reduction and evacuation steps, hydrogen was dosed on the sample at the desired temperature and pressure and the NMR spectra were acquired. To study hydrogen-on-metal resonance, 200-1000 scans were acquired using a recycle time of 0.4 s. Hydrogen-on-support resonance was monitored separately by acquiring 10 scans with a recycle time of 50 seconds to restore full equilibrium magnetization. The absolute intensities of NMR peaks were obtained by comparing the signal intensity with a water reference sample of known spin count. The water sample was sealed in a capillary tube of the length of the catalyst samples to account for the inhomogeneities in the pulse lengths along the probe coil (8).

RESULTS AND DISCUSSION

The irreversibly bound hydrogen on Ru (H_{irr}/Ru) amounts obtained from NMR spectroscopy largely disagreed from those obtained from volumetric chemisorption measurements (Fig. 1). The H_{irr}/Ru amounts obtained from the standard volumetric chemisorption technique showed a steady decrease as a function of reduction temperature, while the H_{irr}/Ru amounts obtained from ^{1}H spin counts of the hydrogen-on-metal resonance did not change appreciably over the same reduction temperature range. The H_{irr}/Ru amounts obtained from the room temperature volumetric hydrogen chemisorption technique approached, but was never equal to, the values obtained from ^{1}H NMR measurements with increasing reduction temperatures. Since no change was observed in the H_{irr}/Ru amounts obtained from ^{1}H NMR measurements, the decrease in the H_{irr}/Ru ratios obtained from volumetric measurements were attributed to a decrease in the amount of the irreversibly bound spilled over hydrogen (H_{irr-sp}/Ru) amounts but not to a change in the particle size. The decrease in the H_{irr-sp}/Ru amounts were correlated with a decrease in the support hydroxyl group resonances with the reduction temperature (9).

Previously, Wu *et al.* (8) reported a closer agreement between the results of the volumetric chemisorption and ^{1}H NMR spin counting techniques in determining the H_{irr}/Ru amounts of Ru/SiO$_2$ catalysts reduced at 723 K. In this work, we observed that under similar conditions, the H_{irr}/Ru amounts obtained
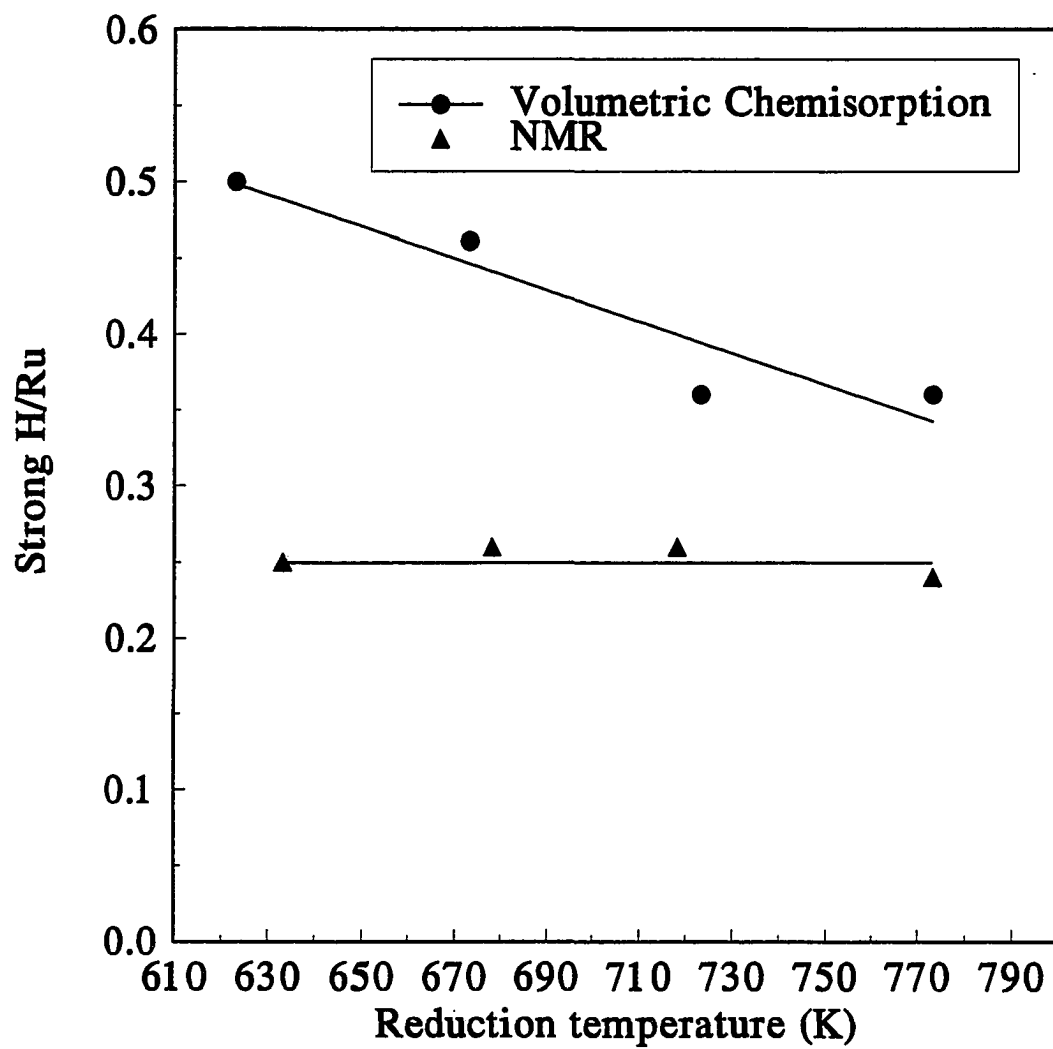
Figure 1. H_{irr}/Ru amounts obtained from ^{1}H NMR and volumetric hydrogen chemisorption measurements

from ^{1}H NMR spin counting was approximately 30% less than the results of the

standard volumetric chemisorption technique. The discrepancy between the two

studies was due to a hydroxyl resonance with a FWHM of 10 kHz (9). Improved

analytical techniques allowed us to identify and account for a broad peak under the

3 ppm resonance (9). The closer agreement observed in the previous studies (8)

was due to the contribution of this resonance to the intensity of the H/Ru

resonance.

Direct NMR Evidence for an Irreversibly Bound Spilled over Hydrogen

The quantitative evaluation of the spilled over hydrogen via ^{1}H NMR

spectroscopy was very difficult because the spilled over hydrogen has similar

resonance frequencies of support hydroxyl groups (0-3 ppm from TMS). However,

they constitute only 3-4% of the total intensity at that resonance. Therefore, to

obtain direct quantitative evidence for the spilled over hydrogen, we needed to

suppress the intensity of the hydroxyl groups by deuterium exchange. The

deuterium exchange was carried out in-situ under D_2O vapor and D_2 gas. A

reduced and evacuated catalyst sample (Ru/SiO$_2$(II)) was first exposed to 15 torr

of D_2O vapor at room temperature. The temperature was gradually increased to

383 K while 500 torr of D_2 was dosed. After fifteen min., the D_2O + D_2 mixture

was replenished. This procedure was repeated twice and the gases were

evacuated. The temperature was gradually raised to 623 K under 500 torr D_2.

The sample was kept at this temperature for two hours. Meanwhile, D_2 gas was

replenished every 10 min. After two hours, more than 90% of the protons in support hydroxyl groups were exchanged with deuterium. This sample was evacuated at 623 K for 1 hour and overnight at room temperature. Due to the long spin-lattice relaxation times of the hydrogen-in-the support resonances, NMR spectra were obtained by accumulating only 10 scans at a repetition time of 50 s. Prior to the introduction of hydrogen, the NMR spectrum of the support hydroxyl groups was taken. The NMR spectrum of the spilled over hydrogen was obtained by subtracting the intensity of the OH resonances prior to the introduction of hydrogen from the fully relaxed NMR spectra under hydrogen atmosphere. In Fig. 2, the NMR spectra of the sample under 20 torr of hydrogen (spectrum A) and after evacuating the sample for 10 min. to a pressure of 10^{-5} torr (spectrum B) were shown. In these spectra, the upfield (-60 ppm) and downfield (3 ppm) resonances were due to the hydrogen chemisorbed on the metal and the spilled over hydrogen species, respectively. Upon introduction of hydrogen, -60 ppm resonance appeared and the intensity of the 3 ppm resonance increased simultaneously. It should be noted here that the residual intensity of the 3 ppm resonance was present even after evacuation to 10^{-5} torr for 10-30 min. which was due to an irreversibly bound spilled over hydrogen.

The time dependency of hydrogen chemisorption and spillover at room temperature was also monitored via in-situ ^{1}H NMR spectroscopy. The hydrogen-on-metal and spilled over hydrogen amounts were obtained by proton
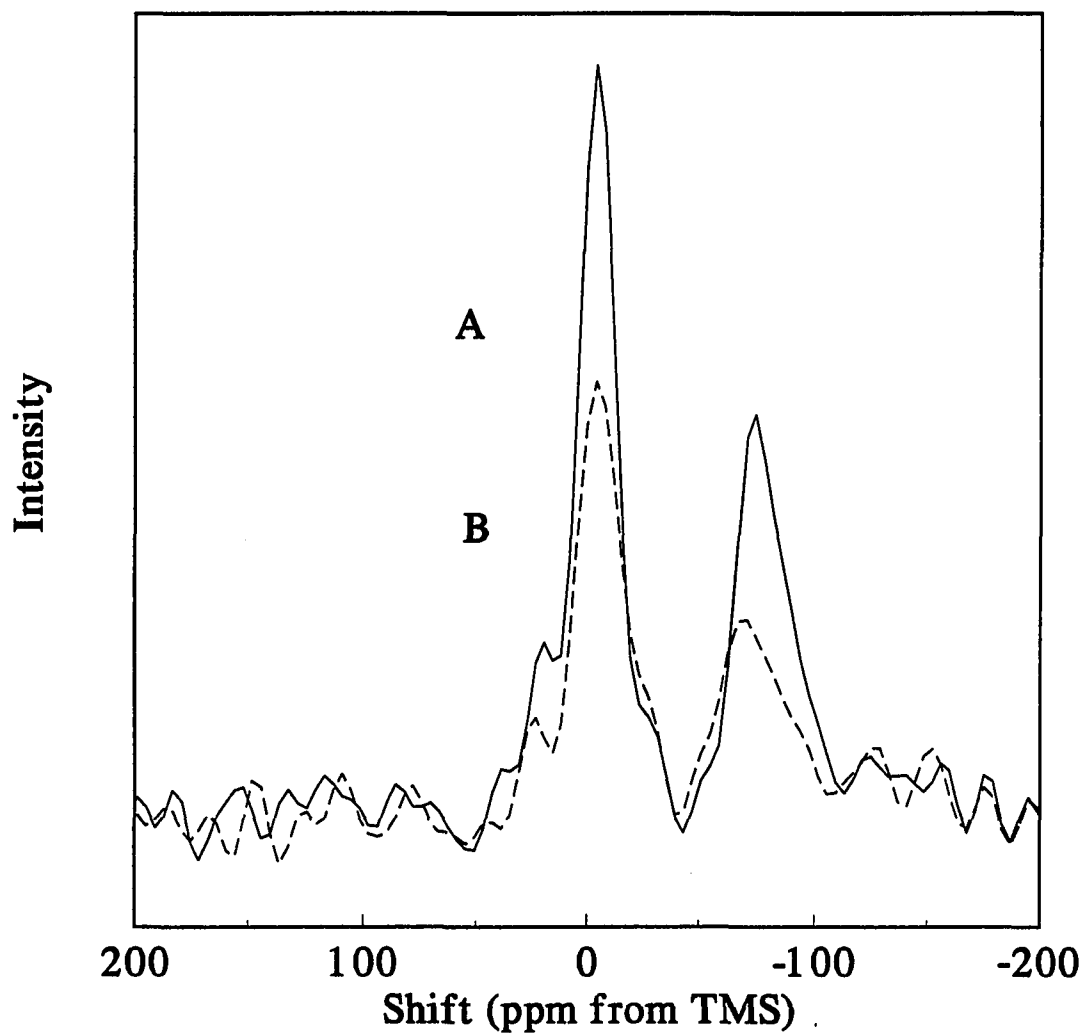
Figure 2. NMR spectra corresponding to a reduced sample (A) under 20 torr of hydrogen and, (B) with irreversibly bound hydrogen. The spectra were obtained by accumulating 10 scans at a repetition rate of 50 s and subtracting the NMR spectrum of the sample under vacuum. The ^{1}H NMR measurements were done after deuterium exchange of the support hydroxyl groups

spin counting of the -60 ppm resonance and the change in the intensity of the 3 ppm resonance, respectively. After 30 min., the sample was evacuated and the time dependency of the -60 ppm and 3 ppm resonances were followed. The quantitative comparison of the NMR measurements with the volumetric chemisorption data is given in Fig. 3. The H/Ru amounts obtained from the sum of the hydrogen-on-ruthenium and spilled-over-hydrogen resonances normalized per ruthenium atom agreed very well with the H/Ru amounts obtained from the volumetric chemisorption measurements for both total and the strong hydrogen amounts. This indicated that the strong H/Ru amounts obtained from the room temperature volumetric chemisorption measurements were overestimated due to the presence of the irreversibly bound spilled over hydrogen. The desorption curve shown in Fig. 3 clearly indicates that evacuation for 10-30 min at room temperature is not sufficient to remove all of the spilled over hydrogen from the support surface. To eliminate the interferences from the irreversibly bound spilled over hydrogen, volumetric hydrogen chemisorption technique was optimized for hydrogen exposure time, adsorption temperatures and evacuation periods. The optimum conditions were obtained from in-situ ^{1}H NMR spectroscopy measurements. In the next sections, the selection of these parameters will be discussed.

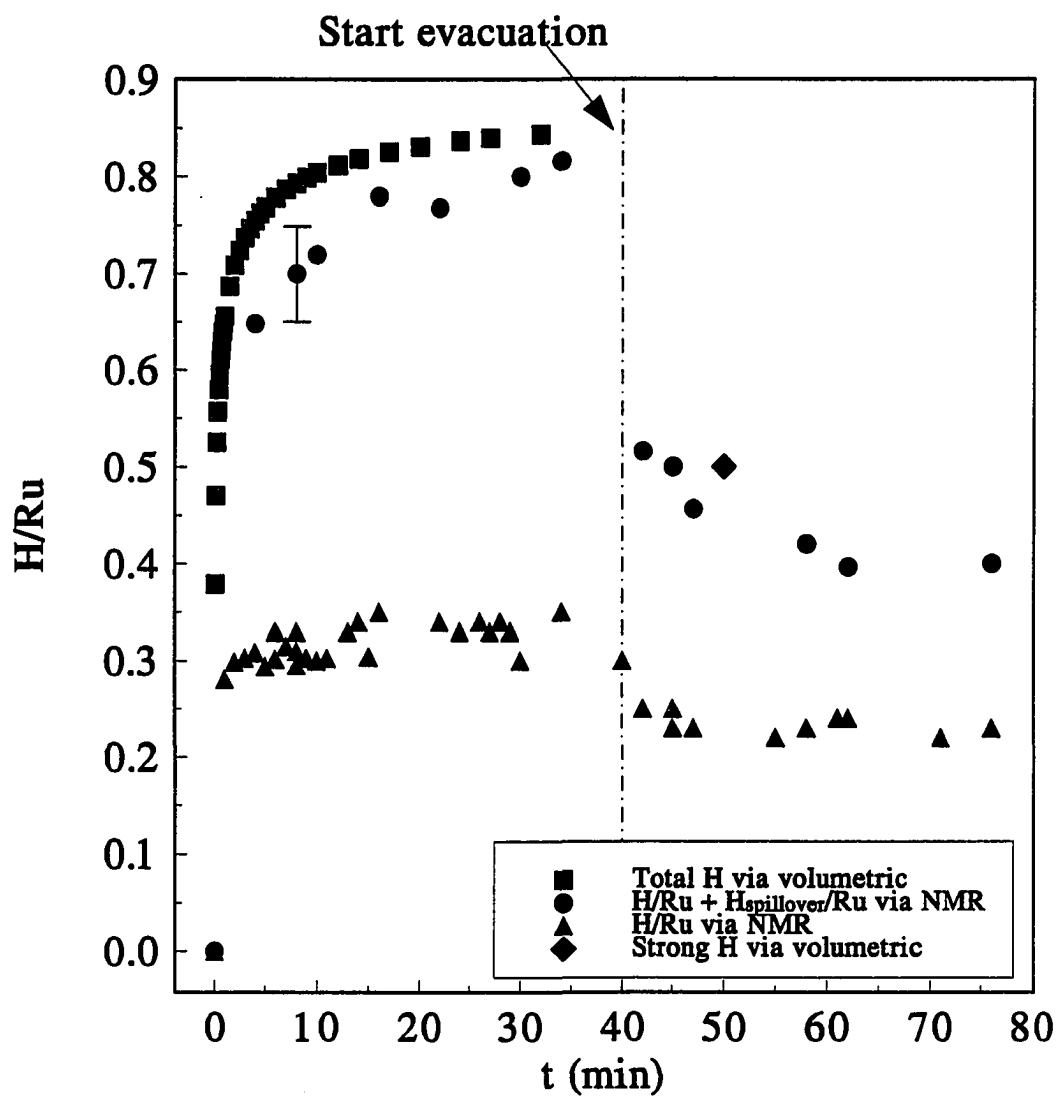Figure 3. The quantitative comparison of hydrogen chemisorption and the spillover process at room temperature and under 19 torr H_2 on $Ru/SiO_2(II)$. The catalyst was reduced at 623 K

Optimization of the Experimental Parameters

The kinetics of hydrogen chemisorption on the metal monitored with *in situ* proton NMR spectroscopy indicated that the hydrogen chemisorption on the metal reached equilibrium within 10 minutes of exposure (Fig. 3). The rate of hydrogen spillover was comparable to the rate of hydrogen adsorption on the metal surface at the beginning of the process. The hydrogen spillover continued at a slower rate as the adsorption progressed. The slower component of the spillover process was attributed to the diffusion limited motion of the spilled over hydrogen on the silica surface (3, 5). To minimize the errors associated with the slowly diffusing component of the spilled over hydrogen, the hydrogen exposure times in volumetric chemisorption technique was limited to 10-15 min.

The effect of temperature on the amounts of hydrogen chemisorbed on the metal was also monitored via NMR spectroscopy. There was no significant change in the total H/Ru amounts over a temperature range of 294-350 K as shown in Fig. 4. Strong H/Ru amounts decreased slightly over the same temperature range. This decrease was partly due to decreased hydrogen amounts. The errors associated with the quantitative analyses of the spectra were lower at higher temperatures due to the narrower linewidths of both hydrogen-on-metal and hydrogen-in-support peaks. An increase in the temperature, however, influenced the amount of spilled over hydrogen substantially as shown in Fig. 5. The decrease in the amount of spilled over hydrogen was attributed to

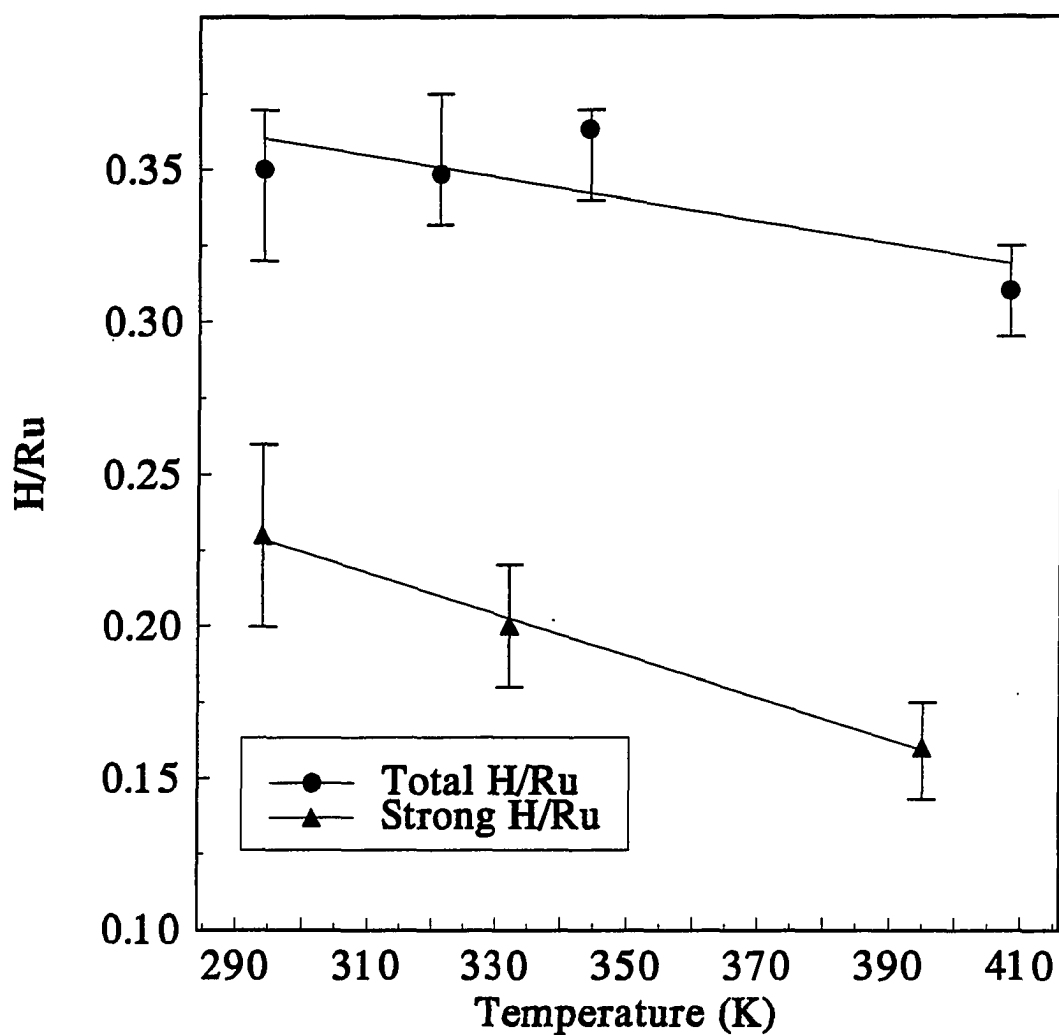Figure 4. The effect of temperature on the H/Ru amounts obtained from ^{1}H NMR spin counting. The total H/Ru amounts were obtained under a hydrogen pressure of 20 torr. The strong H/Ru amounts were obtained after evacuation for 10 min
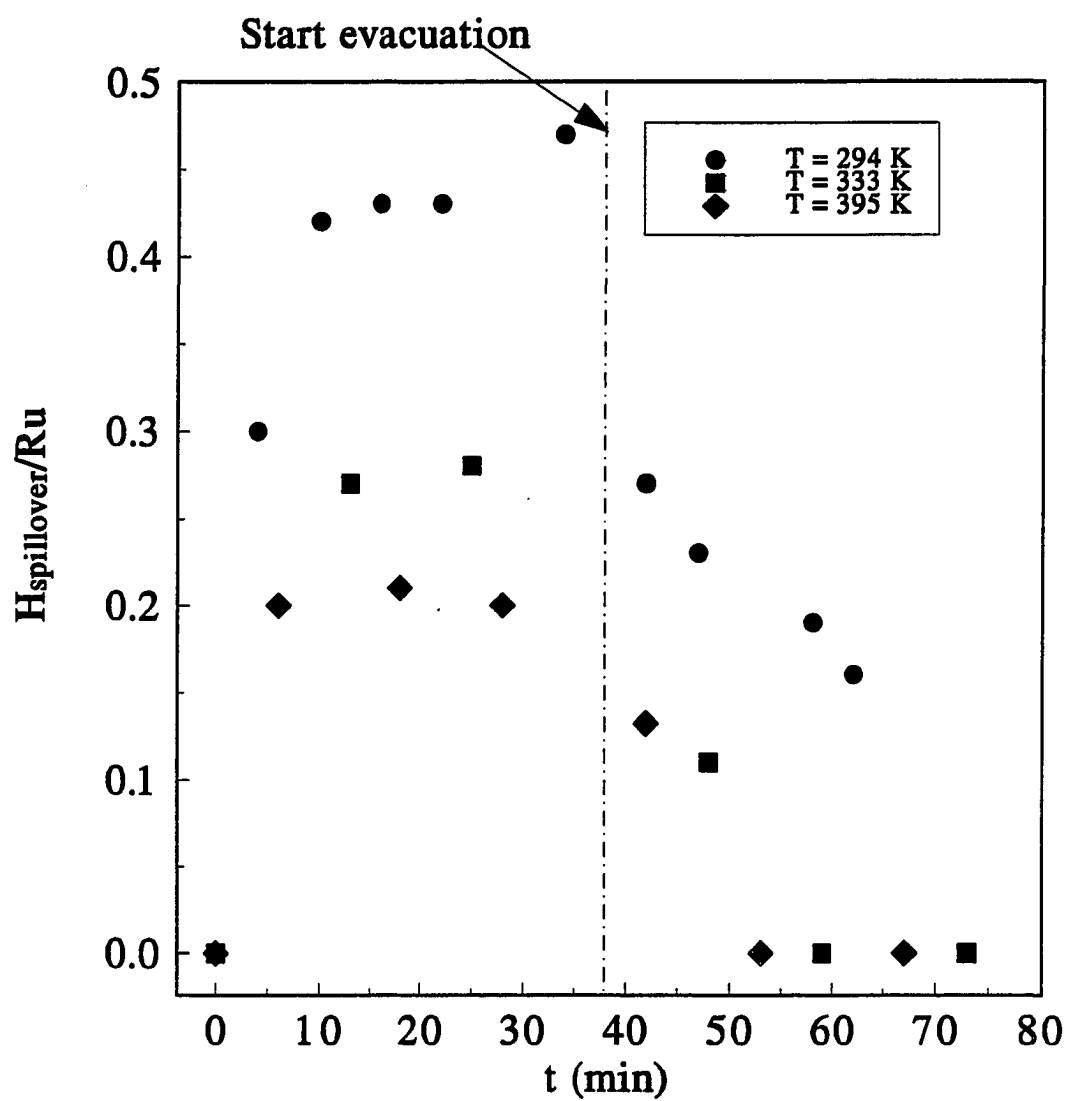
Figure 5. The temperature dependency of the spilled over hydrogen amounts normalized per Ru atom on Ru/SiO$_2$(II) obtained by spin counting proton resonances from *in situ* NMR spectroscopy

the inhibition due to the enhanced selectivity of adsorption at higher temperatures (11). In addition, the removal of the spilled over hydrogen was easier at higher temperatures due to the higher mobility of the adsorbed species (Fig. 5). Within 10 min., almost all of the spilled over hydrogen was removed. Therefore, at higher adsorption temperatures, the accuracy of the volumetric chemisorption can be improved with the enhanced removal of the spilled over hydrogen during the evacuation step prior to the measurement of the weakly bound hydrogen adsorption isotherm.

The H_{ir}/Ru amounts for 3 different catalysts were obtained from the volumetric technique modified as follows:

(i) The measurements were done at 363 ± 10 K,

(ii) The hydrogen exposure times were limited to 10 min. for each hydrogen dose,

(iii) The evacuation period between the total and the strong hydrogen adsorption isotherms was selected as 10 min.

The comparison H_{ir}/Ru ratios obtained from the volumetric chemisorption technique described above with the standard volumetric chemisorption technique and the ^1H NMR measurements are given in Table 1. As seen in the table, the ^1H NMR spin counting and the optimized chemisorption technique yield very close results even for the catalysts reduced at 623 K.

Table 1. The comparison between the H_{ir}/Ru ratios obtained from ^{1}H NMR spin counting, the standard and the optimized volumetric chemisorption techniques. The catalysts were reduced at 623 K

Catalyst	Ru wt%	Standard volumetric	Optimized volumetric	^{1}H NMR spin counting
Ru/SiO$_2$(I)	4	0.18	0.13	0.09
Ru/SiO$_2$(II)	4	0.50	0.28	0.25
Ru/SiO$_2$(III)	10	0.15	0.02	0.03

Although 10 min. was selected as the period of evacuation prior to the determination of the weakly bound hydrogen adsorption isotherm, it must be noted here that the amount of hydrogen that was left on the surface depends not only the hydrogen-metal bond strength and the adsorbed hydrogen amounts but also on the conductance of the vacuum line. Therefore, caution must be exercised whenever the metal dispersion information obtained from the volumetric chemisorption experiments are used to get the turnover frequencies in the catalytic performance measurements.

CONCLUSIONS

An irreversibly bound spilled over hydrogen species was identified on the silanol support, which clearly interfered with the accurate dispersion values measured via a volumetric hydrogen chemisorption technique. The amount of irreversibly bound spilled over hydrogen was a strong function of the catalyst reduction temperature, hydrogen adsorption temperature, and the exposure period. The volumetric chemisorption experiments was optimized to minimize the presence of the irreversibly bound spilled over hydrogen. The optimum parameters were determined for Ru/SiO_2 catalysts. The volumetric chemisorption experiments should be carried out at 363-400 K, at low pressure ranges (10-100 torr) and within short equilibration periods (10 min. for each hydrogen dose). The evacuation period before the weak hydrogen adsorption measurements was determined as 10 min. which was sufficient to remove the spilled over hydrogen without significantly influencing the strong H/Ru ratios.

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ACKNOWLEDGEMENTS

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PAPER 6. THE NATURE OF THE SPILLED OVER HYDROGEN IN Ru/SiO$_2$ CATALYSTS

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ABSTRACT

Quantitative NMR measurements of the hydrogen-on-metal and hydrogen-on-support resonances indicated the existence of both reversibly and irreversibly bound hydrogen spilled over to the silica support. The irreversibly bound hydrogen on the support caused a large discrepancy between the dispersion values measured by ^{1}H NMR and volumetric techniques. The absence of a change in the Knight shift of the hydrogen-on-metal resonance indicated that atomic hydrogen spilled over on the support. However, the spilled over hydrogen did not form O-H or Si-H bonds on the silica surface. Both reversibly and the irreversibly bound spilled over hydrogen possessed a high mobility as indicated by the decrease in the spin lattice relaxation times of the protons in the silanol groups.

INTRODUCTION

Spillover of hydrogen has been studied over 3 decades since the phenomenon was first noted (1-2). Despite the numerous efforts, the process is not very well understood due to the difficulties in identifying the nature of the spilled over species and the interaction between the spilled over hydrogen and the support surface. The rate of the spillover process is believed to be controlled by the diffusion of the hydrogen on the support surface. For example, on carbon supported Pt, the kinetics of hydrogen adsorption on Pt was observed to be very fast and the slow overall kinetics was due to the diffusion of "the spilled over" hydrogen on carbon support (1). The diffusion coefficient of the spilled over hydrogen from platinum on alumina was reported to be $1*10^{-15}$ cm^2/s (3). This and similar studies indicated that the diffusion of dissociated hydrogen on surfaces such as carbon (1), alumina (3) and on titania (4) has energies of activation of 25-30 kcal/mol which was too high for a mere physical migration; so that bond braking and formation had to be involved in hydrogen transfer on the surface (4). Robell et al. (1) noticed that the spillover was taking place more readily at the beginning which indicated that the support sites closer to the metal particles were saturating faster, and the diffusion out of these regions into the bulk of the support was slow. Similarly, Cavanagh and Yates (5) observed that the H-D exchange on Rh/Al$_2$O$_3$ took place faster on the OH groups nearby Rh particles.

NMR spectroscopy has been successfully used to characterize the supported metal catalysts (6-8). Wu *et al.* (6) identified a weakly bound spilled over hydrogen species on silica support by using NMR spectroscopy. Their quantitative measurements on hydrogen-on-metal resonance agreed well within the error limits of experimentation for the strongly bound hydrogen. However, quantitative evaluation of NMR spectra for the weakly bound species was less than that of obtained from chemisorption. Basing on this as well as the supporting evidence form the change in the spin lattice relaxation times of the support protons, they identified a weakly bound spilled over atomic hydrogen on the support. Lenz *et al.* (9) also used NMR spectroscopy to characterize the type of the spilled over hydrogen as well as the nature of the sites created on the silica surface by the spilled over hydrogen. Among three types of hydrogen species postulated in literature that could spill over, namely protonic hydrogen, H^+, hydrogen radical, $H\cdot$, and trihydrogen, H^+_3 (10), they supported the idea of hydrogen radical as the spilled over species.

In paper V, the author reported direct spectroscopic evidence for a strongly bound component of the spilled over hydrogen. Here, a more detailed discussion for the nature of the spilled over hydrogen and its interactions with the silica surface will be given.

METHODS

Catalyst Preparation

The catalyst used in this work was prepared via an incipient wetness technique

using a ruthenium nitrosyl nitrate (26% Ru, Johnson-Matthey) salt as the metal

precursor. A 4 wt% catalyst was prepared from the ruthenium nitrosyl nitrate by

dissolving appropriate amount of salt in 2.2 ml water/g support. A slurry was

prepared by impregnating the support (Cab-O-Sil HS5) with this solution. The

slurry was dried in air at 383 K for 8 hours. The final catalyst was reduced in

flowing hydrogen at 723 K for 2 hours and washed in boiling water to remove

impurities.

NMR Experiments

The *in situ* ^{1}H NMR experiments were carried out in a home built spectrometer

and a home built probe which could operate between 100 and 800 K. About 100

mg of catalyst was placed in the sample chamber of the in-situ probe which was

connected to the glass manifold. First, the sample was heated up to 380 K under

He atmosphere and evacuated to remove the moisture. The reduction was carried

out at 623 K under hydrogen atmosphere which was replenished every 30 min. for

a total of 2 hours. Then the sample was evacuated at the reduction temperature

for 4 hours and at room temperature overnight. Finally, the hydrogen was dosed

on the sample at the desired temperature and pressure and the NMR spectra were

acquired. To study hydrogen-on-metal resonance, 200-1000 scans were acquired

using a recycle time of 0.2 s, which was sufficient to restore full equilibrium magnetization. Hydrogen-on-support resonance was monitored separately by acquiring 10 scans with a recycle time of 50 seconds. The absolute intensities of NMR peaks were obtained by comparing the signal intensity with a water reference sample of known spin count. The water sample was sealed in a capillary tube of the length of the catalyst samples to account for the inhomogeneities in the pulse lengths along the probe coil (6).

RESULTS

In situ ¹H NMR spectroscopy was used to monitor the kinetics of hydrogen

chemisorption on Ru/SiO_2. The quantitative measurements done after exchanging

the support hydroxyl groups with deuterium were reported elsewhere (11). The

NMR measurements were done by acquiring 1000 scans at a recycle time of 0.2 s

unless otherwise noted. The NMR spectrum of the catalyst prior to hydrogen

exposure comprised of only the resonance associated with the support protons (~3

ppm from TMS). This spectrum was subtracted from NMR spectra of the catalyst

sample under hydrogen atmosphere and plotted in Fig. 1 (difference spectra). The

quantitative comparison for hydrogen chemisorption obtained from *in-situ* NMR

spectroscopy to that of volumetric measurements under a pressure of 20 torr and

at room temperature are given in Fig. 2. The curve representing H/Ru obtained

from *in situ* NMR results indicated that the metal surface saturated within 10 min

after the hydrogen was dosed. However, the volumetric measurements indicated

that the adsorption continued slowly over extended periods of time. The difference

NMR spectra taken during the evacuation period (Fig. 3) indicated that the

intensity loss of the hydrogen-on-metal and hydrogen-on-support resonances

proceeded at the same slow rate. After evacuation for 10-20 min (typical

evacuation periods to eliminate weakly bound hydrogen) at room temperature, both

3 ppm and 60 ppm resonances were observed in the difference spectra. The
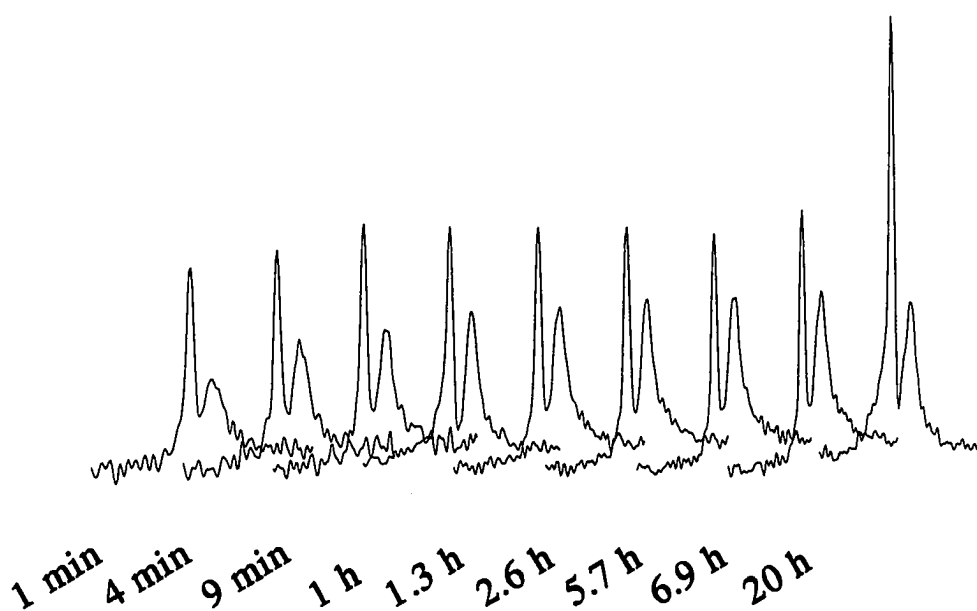
Figure 1. Time dependency of hydrogen chemisorption on Ru/SiO$_2$ under 20 torr pressure and at room temperature

Figure 2. The time dependency of the hydrogen chemisorption on Ru/SiO$_2$ obtained by spin counting the hydrogen on metal resonance from *in situ* NMR spectroscopy and from volumetric hydrogen chemisorption. Both measurements were done at room temperature and under a hydrogen pressure of 20 torr

*2 hours at 120°C + 5.3 hours at 21°C

Figure 3. NMR spectra showing the time dependency of desorption at room
temperature after hydrogen chemisorption at room temperature and
under 20 torr hydrogen for 20 hours

difference spectrum of the sample taken after evacuation for 2 hours at 393 K and 5.3 hours at room temperature had neither hydrogen-on-metal nor hydrogen-on-support resonance. The same experiment carried out at room temperature and under a hydrogen pressure of 87 torr indicated a similar behavior for adsorption and desorption (not shown).

The effect of temperature on hydrogen chemisorbed on Ru and spilled over hydrogen was also investigated by monitoring hydrogen chemisorption at 326 and 400 K via volumetric and NMR techniques. The hydrogen on Ru amounts were evaluated from the spin counting the NMR intensity of the hydrogen-on-metal resonance and the results were compared with the volumetric chemisorption data obtained at the same temperature. The results are shown in Fig. 4 (T= 326 K) and Fig. 5 (T=400 K). The data in Figs. 4 and 5 indicate that the H/Ru amounts did not change significantly with increasing temperature, however, the amount of the spilled over hydrogen decreased.

The T1 measurements on the silanol protons for the pure silica sample indicated that the spin lattice relaxation time of 3 ppm resonance did not change appreciably in the presence of the gas phase hydrogen (Fig. 6). Fitting the inversion recovery data with a mono-exponential function resulted in a T1 of 5.5 s. However, the spin lattice relaxation time of silanol protons in a catalyst sample which was reduced and evacuated to 10^{-6} torr was 11.7 seconds. Upon introduction of 20 torr of hydrogen gas at room temperature, the spin lattice relaxation times of the silanol protons decreased to 5.2 s. After
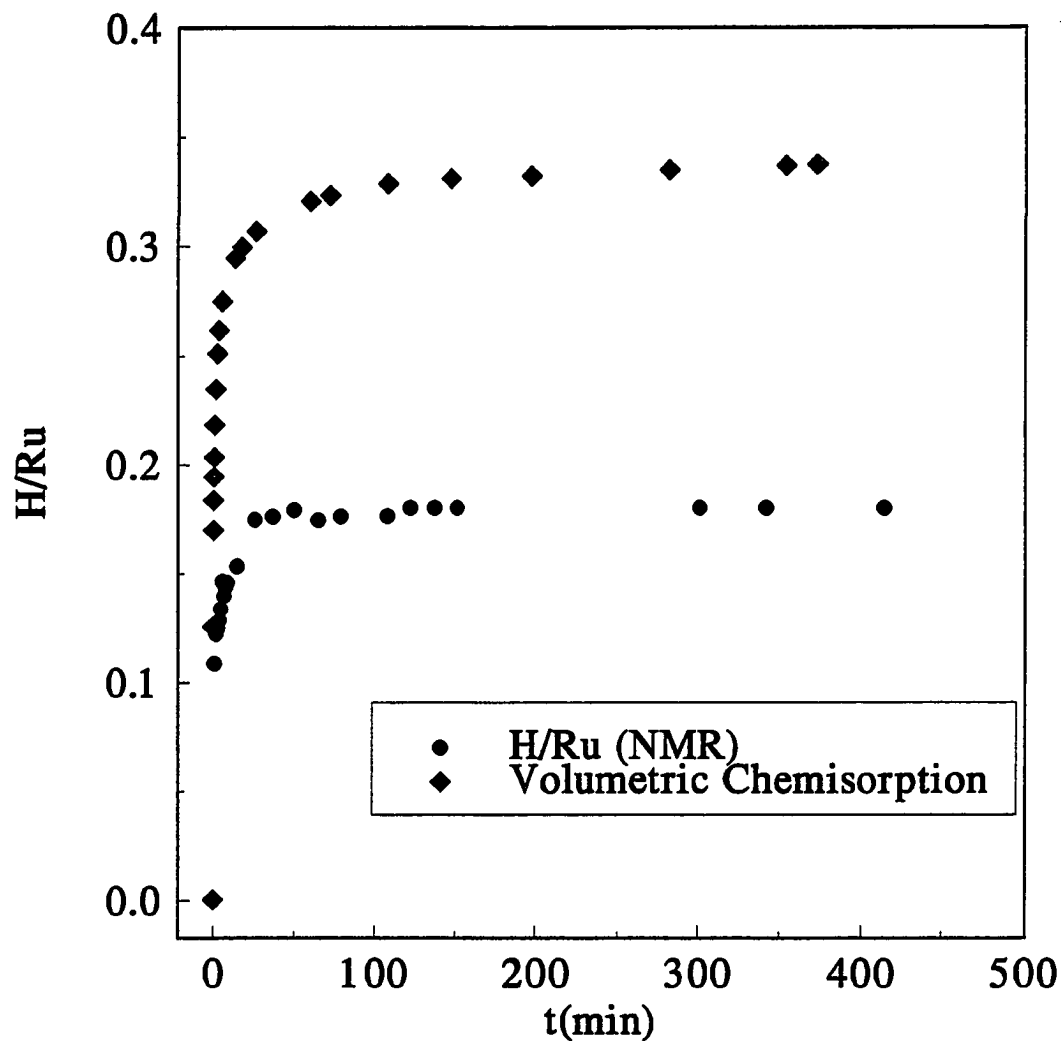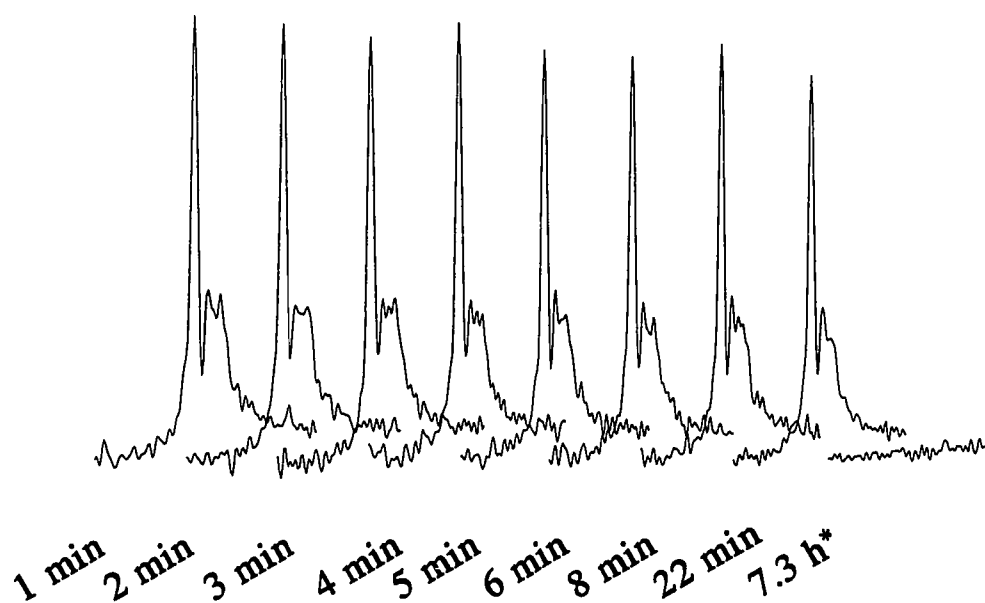
Figure 4. The time dependency of the hydrogen chemisorption on Ru/SiO₂ obtained by spin counting the hydrogen on metal resonance from *in situ* NMR spectroscopy and from volumetric hydrogen chemisorption. Both measurements were done at 326 K and under a hydrogen pressure of 87 torr

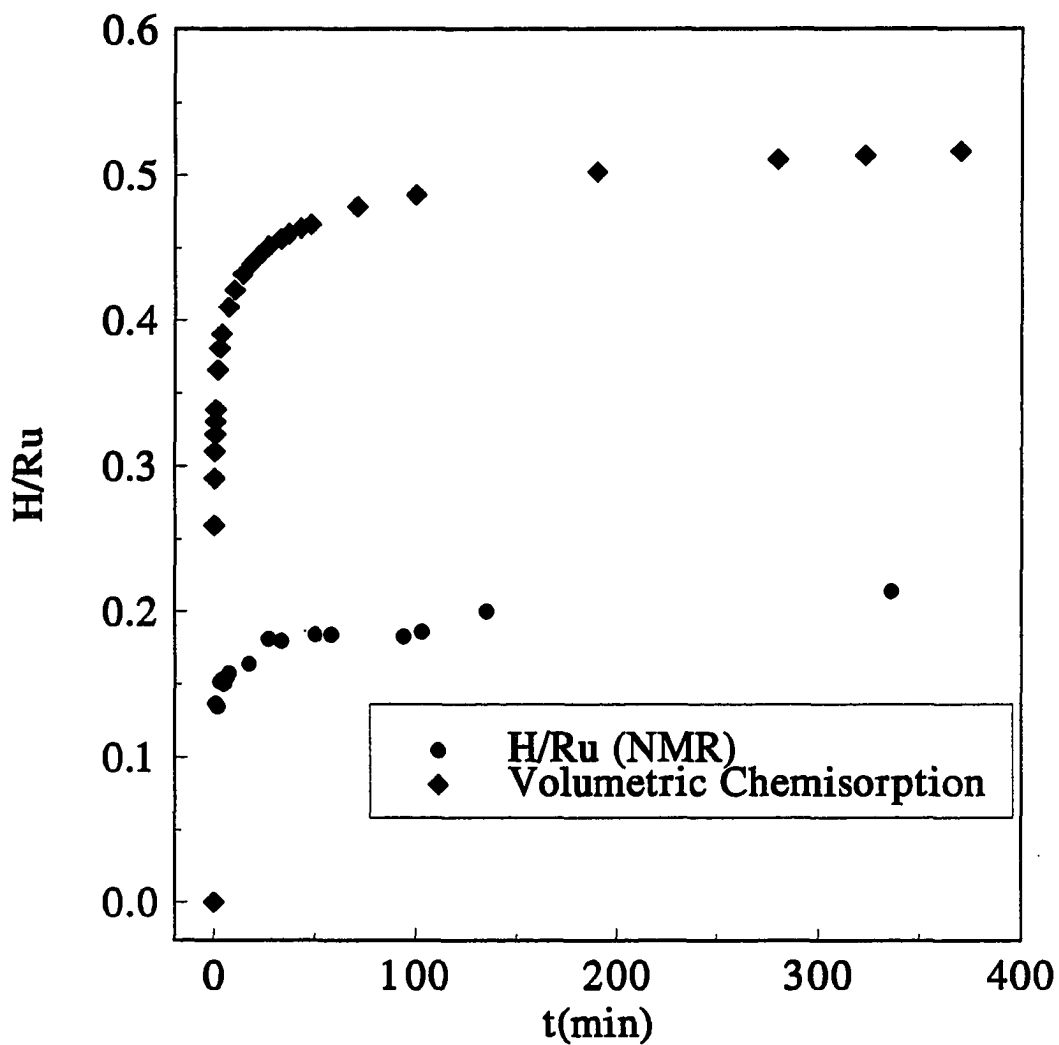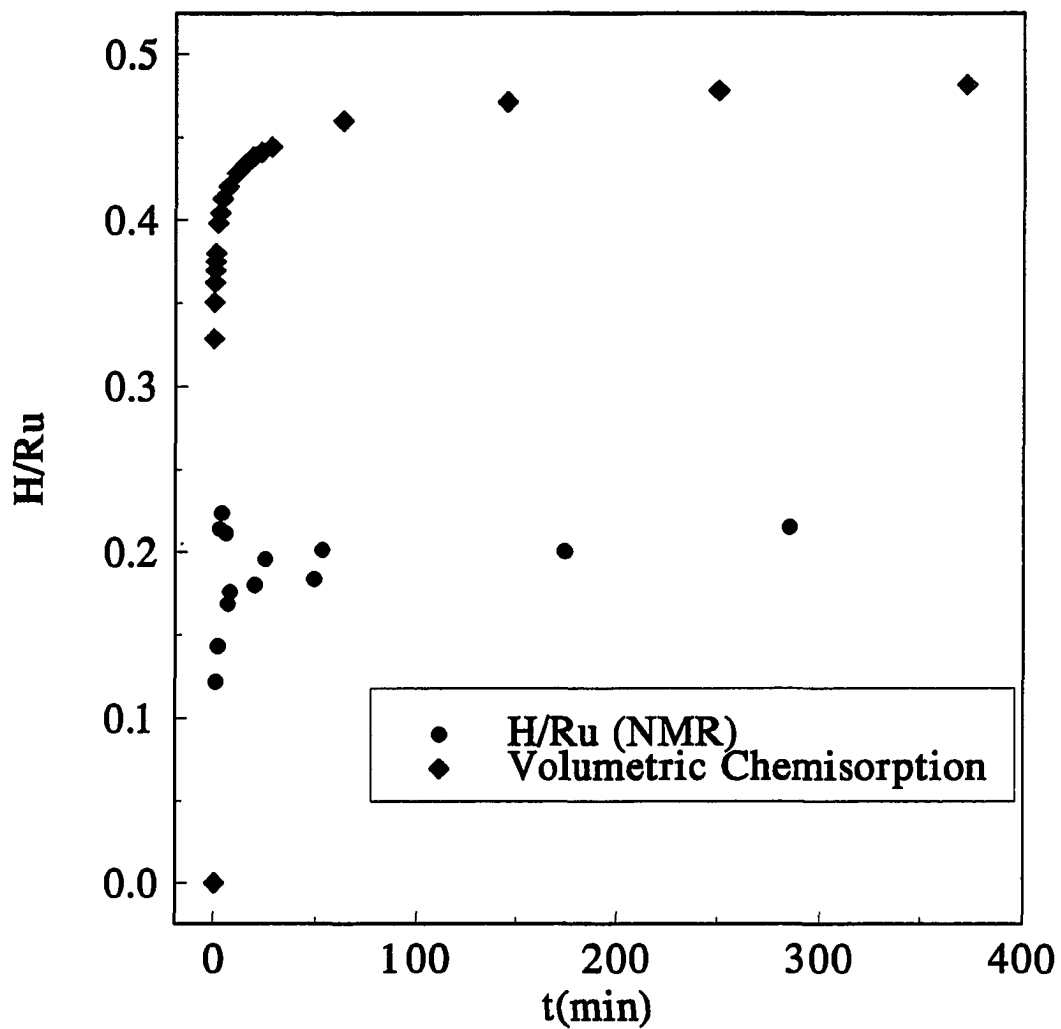Figure 5. The time dependency of the hydrogen chemisorption on Ru/SiO₂ obtained by spin counting the hydrogen on metal resonance from *in situ* NMR spectroscopy and from volumetric hydrogen chemisorption. Both measurements were done at 400 K and under a hydrogen pressure of 87 torr
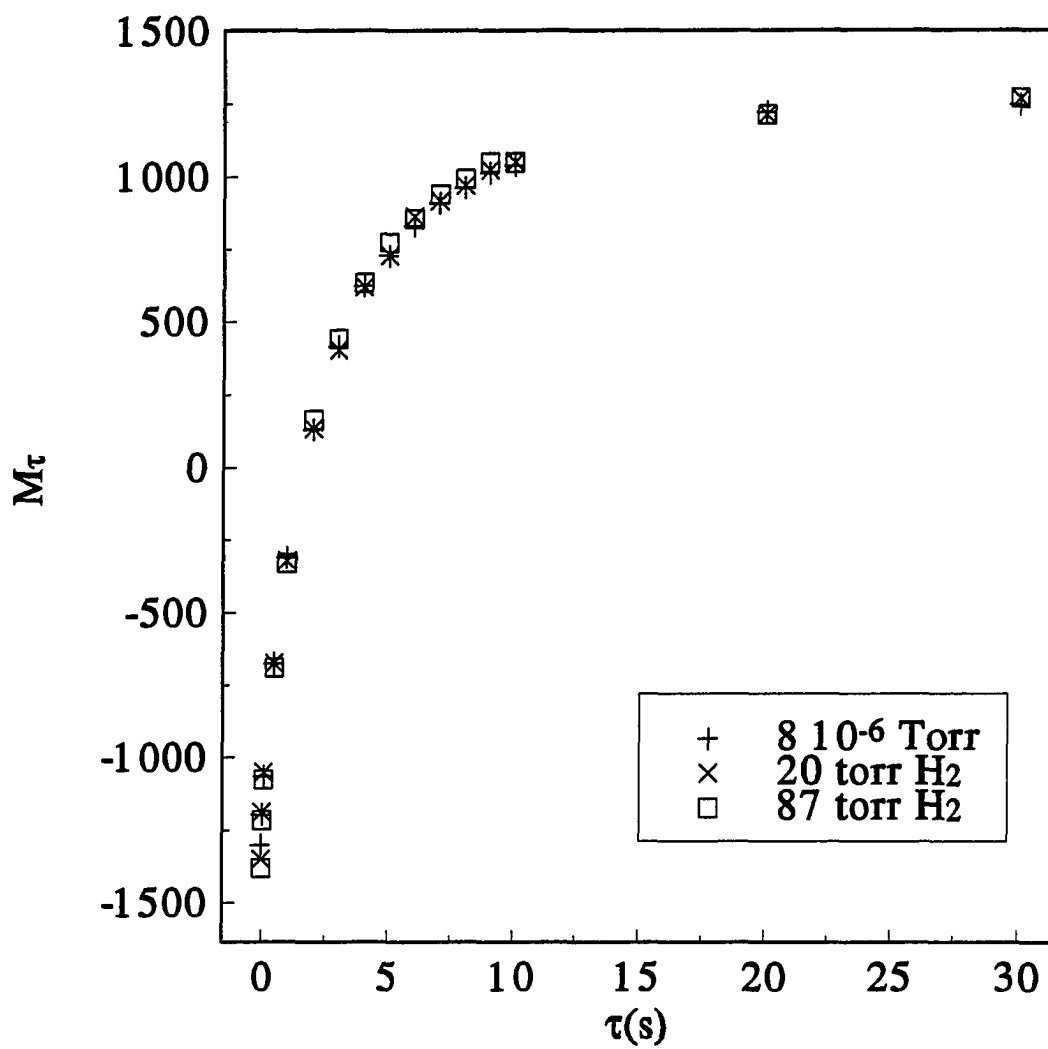
Figure 6. The inversion recovery response of the 3 ppm resonance of a pure silica sample as a function of hydrogen over pressure

Table 1.   T1 of silanol protons at different temperatures and under different hydrogen pressures

Pressure	T1 at 294 K (s)	T1 at 326 K (s)	T1 at 400 K (s)
5 10^{-6} torr	11.7	11.9	10.5
20 torr	5.2	N/A	N/A
Strong H from 20 torr	6.1	N/A	N/A
87 torr	4.8	5.4	4.9
Strong H from 87 torr	7.0	N/A	N/A

the removal of the weakly bound hydrogen by evacuation, the spin lattice relaxation time of the silanol groups increased to 7.2 s which was lower than the corresponding value of a sample without any spilled over hydrogen. The effect of the temperature and hydrogen over pressure on the spin lattice relaxation times of the silanol protons in the catalyst sample is given in Table 1.

DISCUSSION

The kinetics of hydrogen chemisorption on the metal was monitored with *in situ* proton NMR spectroscopy (Figs. 1 and 2). The hydrogen-on-metal resonance reached equilibrium within 10 minutes. The desorption of weakly bound hydrogen from the metal surface was also very fast as shown in Fig. 3. The slow component of the adsorption rates observed during the volumetric experiments was attributed to the spillover process. A comparison of the time dependency of the hydrogen adsorption measured from volumetric techniques and *in situ* NMR spectroscopy shown in Fig. 2 indicated that the hydrogen spillover was a two step process. The kinetics of the fast component of hydrogen spillover was comparable to the rate of hydrogen chemisorption on the metal. The slow component of the spillover process is attributed to the diffusion limited motion of the spilled over hydrogen on the silica surface. In fact, the motion of atomic hydrogen in SiO_2 wafers was reported to be trap limited with a diffusion coefficient of 10^{-14} cm^2/s (12-13). Similar values were obtained for the diffusion coefficient of the spilled over hydrogen on Al_2O_3 (3) and TiO_2 (4) surfaces.

Although the existence of hydrogen spillover is well established (14, 15 and the references therein), the nature of the spilled over species is still debated (8-10). Among the suggested candidates such as bare proton, hydrogen radical and trihydrogen, we prefer to dismiss the bare proton as an alternative. Because, in the case of bare proton, for each spilled over hydrogen species an electron would

be left on the metal surface. These extra electrons on the metal surface are expected to change the Knight shift which was not observed. As suggested by Sheng and Gay (8), atomic hydrogen is more likely to be the spilled over hydrogen species. However, this species interact with the silica surface significantly as indicated from the changes in the spin lattice relaxation times. Furthermore, the resonance due to the spilled over hydrogen in the silica support identified previously (11) has similar linewidths and resonances as the support hydroxyl groups which also suggests closer interactions between the spilled over hydrogen and the silica surface. But this interaction does not involve the formation of strong O-H or Si-H bonds as will be discussed below.

The spin lattice relaxation times, T1, of silanol protons were strongly influenced from the presence and the amount of the spilled over hydrogen. In the absence of Ru metal, i.e. spilled over hydrogen, the spin lattice relaxation times of the silanol protons remained uninfluenced from the hydrogen over pressure (Fig. 6). The decrease in the spin lattice relaxation times suggest the presence of the local fluctuations created by the weak coupling of the mobile spilled over hydrogen to the hydroxyl groups. If the spilled over hydrogen did not interact with the silica surface, the paramagnetic nature of the hydrogen atom would render its resonance invisible to the NMR spectroscopy. But, the author was able to observe the proton resonance due to the spilled over hydrogen quantitatively (11) which indicated that the paramagnetic nature of the atomic hydrogen was not operable here. Although weak couplings may be present, the formation of new OH groups in the presence

of the spilled over hydrogen can not be substantiated. For example, Chesters *et al.* (16) studied the hydrogen spillover process on a Pt/SiO_2 catalyst in the presence and in the absence of spilled over hydrogen via ^1H NMR spectroscopy. They concluded that in the presence of spilled over hydrogen, new OH groups were created in the silica support. The reversibility of the spillover process at lower temperatures observed in the author's work argues against the formation of new OH groups in the presence of the spilled over hydrogen. The difference spectra obtained during the evacuation period after hydrogen chemisorption at room temperature and under 20 torr hydrogen pressure (Fig. 3) had both hydrogen-on-metal and hydrogen-on-support resonances for short evacuation periods. Both of these resonances disappeared after evacuation at 393 K for 2 hours and at room temperature for 5.3 hours which suggested the reversibility of the spillover process. The elimination of silica hydroxyl groups require much higher temperatures (17-20). Therefore, the author does not support the idea of formation of new OH groups. Furthermore, if new OH were formed which were chemically similar to the already existing ones, the T1 of the hydroxyl groups would not be influenced as much as it was observed here. The drastic change in the T1 of the support hydroxyl groups in the presence of spilled over hydrogen suggests chemical differences between the nature of the support hydroxyl groups and the spilled over hydrogen.

Finally, adsorption kinetics data presented in Figs. 4 and 5 indicate that the amount of spilled over hydrogen decreases with increasing temperature while the

amount of hydrogen adsorbed on ruthenium does not change over the same temperature range. Therefore one can conclude that the spillover of hydrogen from ruthenium to the silica surface is more sensitive to the changes in temperature than the hydrogen chemisorption on metal. This was due to enhanced rates of the associative desorption from the support surface at higher temperatures. The effect of temperature on the weakly bound hydrogen (both on the metal and on the support) was also investigated via volumetric chemisorption measurements. Volumetric chemisorption experiments were carried out at different temperatures with a hydrogen exposure time of 10 min. for each dose and an evacuation period of 5 min. before the measurement of the weak hydrogen chemisorption amounts. The results plotted in Fig. 7 indicated a monotonous decrease in the total hydrogen chemisorption value as a function of temperature while the weakly bound hydrogen amounts increased. The decrease in the total hydrogen chemisorption amount with increasing temperatures can be attributed to the effect of the energetics of the spillover process. The increase in the weakly bound hydrogen amounts with temperature suggests a higher degree of mobility of the chemisorbed hydrogen and an enhanced recombinative desorption process. The reversibility of the spillover process upon thermal evacuation suggests that the removal of the strongly bound spilled over hydrogen is kinetically limited. At high temperatures, the mobility of this species within the silica framework increases, so does the probability of finding another hydrogen atom for recombination.
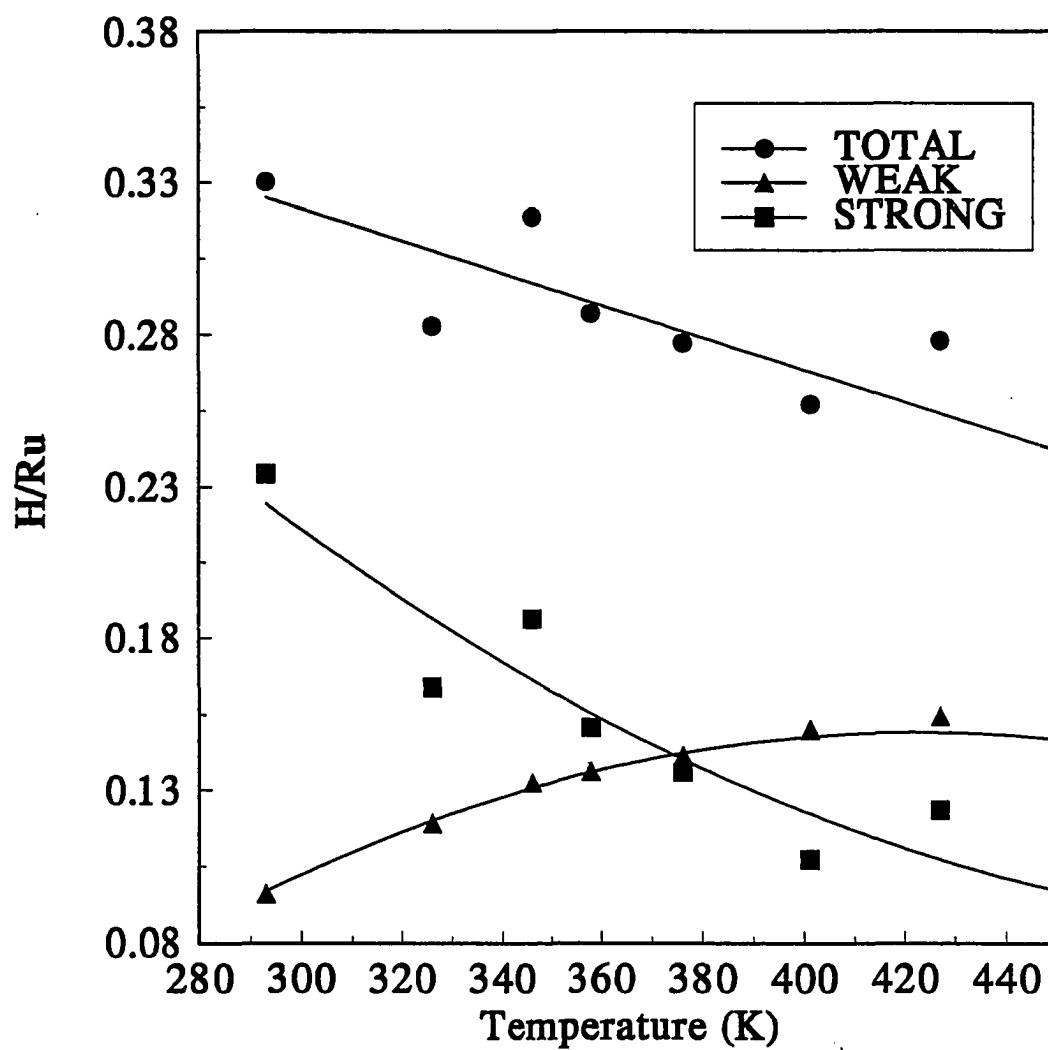
Figure 7. The effect of the temperature on the hydrogen chemisorption as monitored by the volumetric chemisorption technique

CONCLUSIONS

The nature of the spilled over hydrogen was discussed within the context of the ^{1}H NMR spectroscopy evidence. The spillover process did not influence the proton Knight shifts which suggested that the atomic hydrogen must be spilled over. The atomic hydrogen weakly interacted with the silica support such that the NMR resonance due to the spilled over hydrogen exhibited O-H characteristics. However, the reversibility of the process at temperatures lower than that was required for the O-H or Si-(OH) bond breaking indicated the absence of formation of new hydroxyl groups on the silica surface.

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GENERAL CONCLUSIONS

No ^{1}H NMR evidence was found for a through metal electronic interaction between the alkali promoter and the chemisorbed hydrogen in Ru/SiO$_2$ catalysts. Alkali metals exist in an oxide state after catalyst reduction in flowing hydrogen which are not capable of donating electrons to the metal sobstrate. Na and K block hydrogen chemisorption sites, however, Cs is pushed off the surface upon hydrogen chemisorption. The main mechanism of alkali promotion is the restriction of hydrogen mobility even at high temperatures and pressures. This conclusion is consistent with the effects of alkali promoters on the Fischer Tropsch Synthesis.

The support surface is modified significantly in the presence of alkali metals. The interaction of silica support with ruthenium metal and alkali promoters result in a decrease in the density support hydroxyl groups. In addition to the elimination of the OH group protons in the support surface, another proton population with a ^{1}H NMR resonance of about 10-15 ppm downfield from TMS was created in the presence of alkali promoters which was assigned to an alkali hydroxide species present in the silica support.

The interaction of spilled over hydrogen with the silica support monitored via *in-situ* ^{1}H NMR spectroscopy indicated that the adsorption of hydrogen on silica supported ruthenium catalysts is a very fast process. A clean Ru surface saturates within 10 min of the introduction of hydrogen gas. Slow kinetics observed in the literature is due to the hydrogen spillover process. In addition to

the weakly bound spilled over hydrogen, a strongly bound component of the spilled over hydrogen was identified in the silica support. The quantity of this hydrogen population increases with hydrogen pressure, the equilibration period and decreases with the catalyst reduction temperature. The standard volumetric chemisorption technique was modified to eliminate the errors associated with the spilled over hydrogen during the characterization of the metal surfaces.

RECOMMENDATIONS FOR FUTURE WORK

The full understanding of the role of alkali promoters in the Fischer Tropsch synthesis requires carefully conducted mechanistic studies on well characterized catalysts. The significant changes observed in the nature and the densities of the OH groups in the silica support strongly suggests that the supporting oxide may play an important role in the CO hydrogenation chemistry. I recommend the following experiments as the starting point for continued studies:

1. The acidity changes observed in ^{1}H NMR spectroscopy of the OH groups in the silica support should be monitored as a function of metal loading, alkali loading and reduction temperature via microcalorimetric techniques. Ammonia adsorption for the determination of acidic sites and sulfur dioxide adsorption for the determination of the basic sites can be used.

2. The role of the different hydroxyl groups in the silica support on the Fischer Tropsch chemistry has to be investigated. In particular, the effect of the number of the OH groups in the support on the transport properties of the reactants (CO and hydrogen), intermediates (ethylene in particular) and the products should be monitored via residence time, and isotopic tracer studies.

3. The effect of the alkali promoter in the support and on the metal on alkene readsorption has to be investigated via selectivity measurements of the Fischer Tropsch reaction. Effect of the promoter on the selectivity with an alkene/syn-gas co-feed should be monitored for alkali promoted catalysts.

The same studies should be conducted on a mechanical mixture of alkali/support + metal/support to elucidate the role of the alkali on the support on the reaction selectivity.

4. The type of the motion restricted (adsorption/desorption or surface diffusion) in the presence of alkali promoters neeeds to be identified. Mechanistic studies on the Fischer Tropsch chemistry on the metal surfaces with the inclusion of the restricted hydrogen mobility information can help further elucidate the role of alkali promoters in this and other hydrogenation/dehydrogenation reactions.

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