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Hydrogen Chemisorption on Potassium Promoted Supported Ruthenium Catalysts

Deniz O. Uner,* Marek Pruski,† Bernard C. Gerstein,† and Terry S. King*

**Department of Chemical Engineering and Ames Laboratory, Iowa State University, Ames, Iowa 50011-2230;*
†Ames Laboratory, Ames, Iowa 50011-3020

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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. © 1994 Academic Press, Inc.

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 reduces the available surface sites for strong hydrogen and CO chemisorption. However, the existence of electronic interactions induced by the promoter has still not been 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, 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 100–125 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

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hence a change in its acid strength. 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 (1×2) 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 that 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, $Ru(NO)(NO_3)_3$ 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, drying overnight at room temperature, and then drying for 4 h in air at 383 K. The unpromoted catalyst was reduced in flowing hydrogen for 2 h at 623 K. The reduced catalyst had a Ru dispersion of about 10% measured by strong hydrogen chemisorption. After reduction, the 4% Ru/SiO_2 catalyst was impregnated with the potassium nitrate solution of the desired composition such that 2.2 ml of solution per g 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 2 h. 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 of solution (1.5 wt% Ru) per g of support. The amount of potassium nitrate was adjusted to obtain potassium loadings of 33.3, 50, 66.6, and 75 at% 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 into 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 h. After reduction, the samples were evacuated for 4 h 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 h, and evacuated to 10^{-5} Torr for 5 min. 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 a 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 0.2–0.4 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 s to restore the equilibrium magnetization. The spin–lattice relaxation times, *T*1, 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. 1d). Switching to a flowing mixture of 10% hydrogen in helium resulted in a decomposition beginning significantly earlier (Fig. 1c). 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, at which potassium nitrate decomposed. This indicated that the presence of ruthenium catalyzed the decomposition of potassium nitrate.

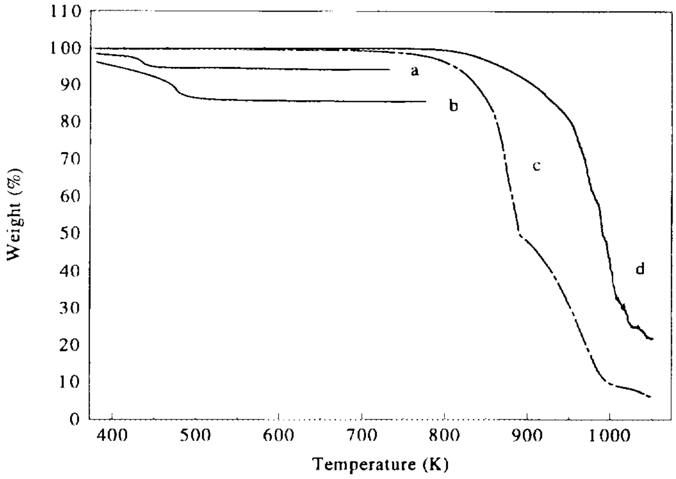

FIG. 1. The results of the thermogravimetric analysis of (a) 4% Ru/SiO_2, (b) 4% Ru/SiO_2 coimpregnated with potassium at a K : Ru atomic ratio of 2 : 1, (c) potassium nitrate in the presence, and (d) in the absence of a reducing atmosphere.

The ^{1}H 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

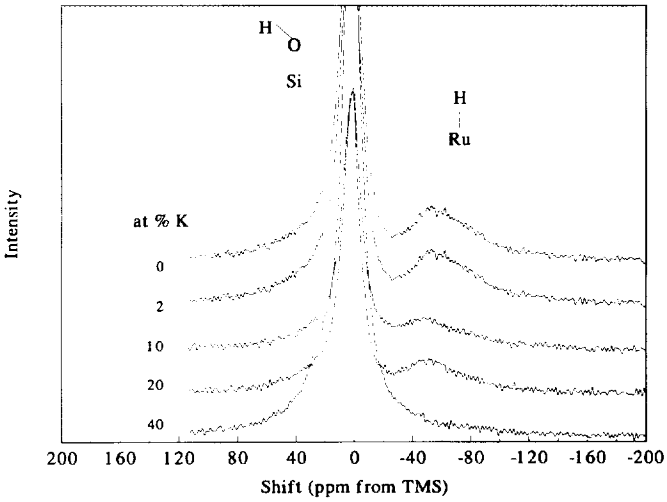

FIG. 2. ^{1}H NMR spectra of sequentially impregnated $K/Ru/SiO_2$ catalysts. Each of the spectra shown is obtained by averaging 1000 scans.

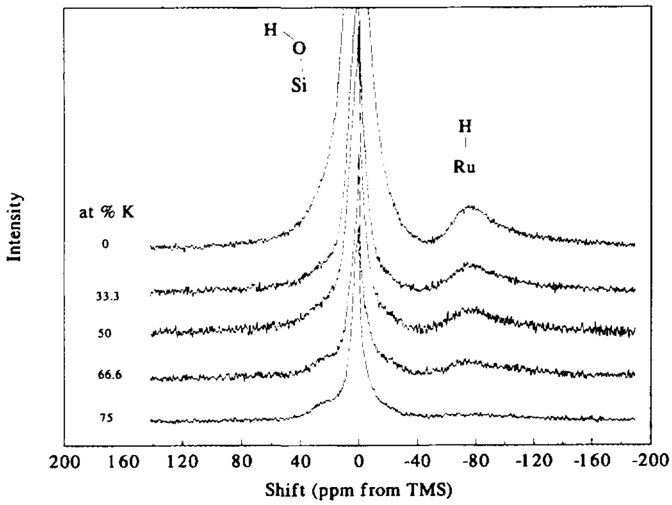

FIG. 3. ^{1}H NMR spectra of co-impregnated K/Ru/SiO$_2$ catalysts. Each of the spectra shown is obtained by averaging 1000 scans.

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 coimpregnated series of catalysts are shown in Fig. 3. In these spectra, a third peak appeared at approximately 20 ppm at potassium loadings of 50 at% 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). Thus, we assume that the 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 now be 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 the potassium-to-ruthenium molar ratio is 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

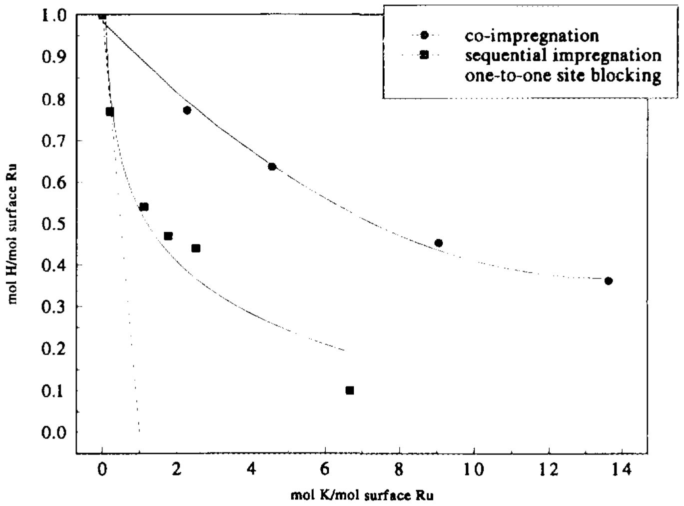

FIG. 5. Change in NMR intensity of the hydrogen-on-metal resonance as a function of alkali loading. The dashed line represents the case in which each alkali atom would have blocked one hydrogen chemisorption site on ruthenium particles.

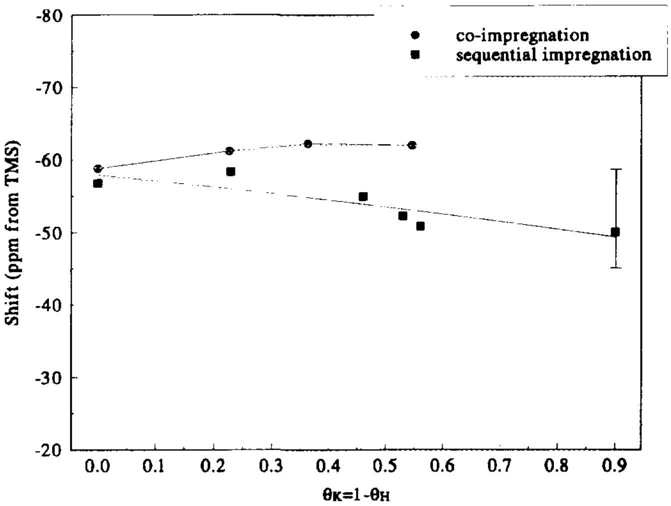

FIG. 4. The change in hydrogen-on-metal resonance as a function of potassium coverage.

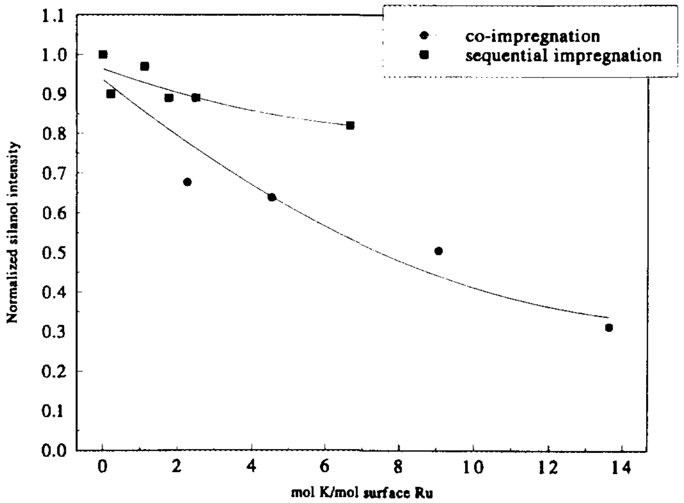

FIG. 6. Change in relative silanol peak intensity as a function of potassium loading. The silanol intensity was normalized with respect to the silanol intensity of the unpromoted catalyst.

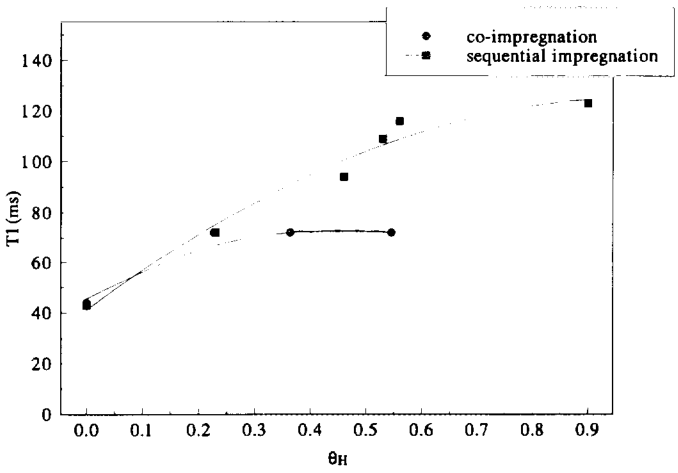

FIG. 7. Spin–lattice relaxation times of hydrogen on metal resonances as a function of surface hydrogen coverage.

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, *T*1, of the strongly bound hydrogen is plotted in Fig. 7 as a function of surface hydrogen coverage. $T1_s$ 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.

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_2O. 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_2O, Cs_2O_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_2O evaporated immediately. Similarly, De Paola *et al.* (34) reported that coadsorption of potassium and oxygen on Ru(001) yielded stable KO_2 andK_2O_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 ^1H 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 ^1H 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 higher temperatures. Their results suggested that 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 low 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 pH 1–2, 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 in which 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 some researchers to postulate that the same mechanism of electron density transfer from the alkali species to the metal particle also holds in supported metal catalysts. 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 coimpregnated 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 regarding 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.

On the basis of this work, we conclude that alkali oxides present in supported metal catalysts are unlikely to donate electron density to the metal particle, consistent with the conclusions of other studies (42, 43, 45). For example, LEED analysis of coadsorbed 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 suggested by Ponec and co-workers (42, 43), the transfer of electron density from a promoter to the metal is not likely to occur to such an extent 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 ^1H 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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