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Adsorption and Reaction of CO and H_2 on K-Promoted Rh/SiO_2 Catalysts

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The adsorption of CO and H_2 on a series of alkali-promoted Rh/SiO_2 catalysts was investigated by IR spectroscopy and volumetric chemisorption. The characteristics of the support as well as the method of addition of the alkali species were found to influence the adsorptive properties of the catalysts. Alkali species on wide-pore Rh/SiO_2 tended to partition to the support and did not interact strongly with the Rh crystallites. When alkali and metal salts were coimpregnated onto a nonporous SiO_2 support, intimate alkali–metal contact resulted in significant electronic interactions between the alkali species and the metal. When alkali species were added to a prereduced Rh/SiO_2 (nonporous) catalyst, a chemical interaction between a tilted adsorbed CO and the alkali species was suggested. The nature and location of the alkali species were suggested to be important parameters in determining the effect of alkali promoters on Rh/SiO_2 catalysts. The rate of CO conversion decreased substantially with promotion for all of the promoted catalysts. An unusually low apparent activation energy was found for the sequentially impregnated (nonporous SiO_2) promoted catalyst, and it was suggested that this might be related to the unusually low frequency peak seen in the IR spectrum of adsorbed CO on this catalyst. © 1987 Academic Press, Inc.

INTRODUCTION

The study of the surface structure and chemistry of supported Rh catalysts has received significant attention in recent years. Rh may catalyze a wide variety of reactions, including CO hydrogenation and hydroformylation. The nature of the reaction products obtained with Rh is often quite sensitive to the environment of the catalyst, making an understanding of its structure and its adsorptive properties imperative in understanding the behavior of the catalyst in these reactions.

Rh catalysts are also sensitive to the presence of additive species such as alkali and early transition metal ions or oxides. Ichikawa and co-workers (*1–4*) have recently investigated the effects of both oxophilic and nonoxophilic transition metal ions on the adsorptive and catalytic behavior of Rh/SiO_2. They found differences in the action of the two types of promoters in both adsorption and reaction studies. Mn, Ti, or Zr present as suboxides were found to interact directly with CO adsorbed on Rh, promoting CO dissociation. Zn, Mg, or Fe ions had a geometric ensemble effect which resulted in selective site-blocking of the Rh surface.

The effects of alkali promoters on the CO hydrogenation activity and selectivity of TiO_2-supported Rh catalysts has been studied by Chuang *et al.* (*5*). They found that the electronic effects of the alkali species were more important than physical blockage of Rh sites. The promoter had different effects on the formation of oxygenate and hydrocarbon products. The alkali species suppressed the hydrogenation ability of the catalyst and enhanced the oxygenate selectivity.

In a recent investigation of alkali-promoted Rh/Al_2O_3 catalysts in this laboratory (*6*) no significant electronic effects of the addition of even high concentrations of al-

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kali salts were found. The effect of the alkali species on the adsorptive properties of the Rh catalyst series was attributed mainly to the blocking of Rh sites by the alkali species. The method of preparation was found to have a significant effect on the degree of the interaction between the alkali additive and the catalyst surface.

Many studies of alkali promotion on both single crystals (*7–10*) and supported metals (*5, 11, 12*), as well as recent theoretical investigations (*13, 14*), have suggested that alkali species may have significant electronic or electrostatic interactions with transition metals which result in modifications in the nature of adsorption of molecules such as CO on these metals. The absence of evidence of such an effect in the alkali-promoted Rh/Al_2O_3 system in our investigation was attributed to the preferential partitioning of a large fraction of the alkali species to the acidic Al_2O_3 support. The study reported herein is an extension of that work to alkali promotion of SiO_2-supported Rh catalysts in an effort to probe alkali–metal interactions in the presence of a more inert support.

EXPERIMENTAL

The adsorption of CO and H_2 on a series of alkali-promoted Rh/SiO_2 catalysts was investigated by IR spectroscopy and volumetric chemisorption. CO/H_2 reaction was also carried out on these catalysts. The characteristics of the SiO_2 support, the level of alkali promotion, and the method of preparation of the catalysts were all varied in these studies.

Catalyst preparation. Catalysts were prepared by aqueous impregnation of two different types of SiO_2 with $Rh(NO_3)_3$ to incipient wetness for a nominal weight loading of 3%. A wide-pore (Strem) and a nonporous (Degussa) silica were used. Both types were high surface area materials. In the case of each support, a large quantity of Rh/SiO_2 was prepared in a single batch which was used to prepare all the promoted catalysts in that series. In this way some characteristics of the final catalysts could be kept constant for each series.

Promoted catalysts were prepared by impregnation of Rh/SiO_2 with KNO_3 in one of two ways. In the first (coimpregnation), the alkali salt was added to the Rh/SiO_2 precursor catalyst *before* decomposition of the $Rh(NO_3)_3$ precursor. In the second method of preparation (sequential impregnation), the supported Rh precursor species was first decomposed and reduced to zero-valent Rh metal prior to a second impregnation with the alkali salt. The alkali salt was then decomposed in a second reduction treatment identical to the first. After preparation, all catalysts were dried in air at 363 K overnight. All catalysts were reduced at 673 K in flowing H_2 for 16 h after a 1 K/min ramp to the reduction temperature. Table 1 describes the catalysts.

Procedures. IR spectra of adsorbed CO and CO_2 were taken using an Analect FX-6200 FTIR spectrometer at a resolution of 2 cm^{-1}. Spectra were generated by coadding 100 scans and subtracting the SiO_2 background. The IR cell and gas handling system were described previously (*6*). In these experiments, the final gas pressure in the IR cell was about 5 Torr.

Volumetric chemisorption measurements were made in the same gas-handling system as the IR pretreatments, using a small volume glass cell. H_2 and CO isotherms were

TABLE 1

Description of Catalysts

Catalyst[a]	Preparation method[b]	Support[c]	Rh : Alkali
I-1 : 0-P	Impregnation	Wide pore	1 : 0
SI-2 : 1-P	Seq. impregnation	Wide pore	2 : 1
SI-1 : 5-P	Seq. impregnation	Wide pore	1 : 5
I-1 : 0-N	Impregnation	Nonporous	1 : 0
CI-2 : 1-N	Coimpregnation	Nonporous	2 : 1
CI-1 : 5-N	Coimpregnation	Nonporous	1 : 5
SI-1 : 5-N	Seq. impregnation	Nonporous	1 : 5

[a] All catalysts are based on 3 wt% Rh.

[b] See text for explanation of preparation methods.

[c] See text for physical description of supports used.

recorded at ambient temperature and 100–400 Torr. Time for equilibration of each point was at least 24 h. Prior to IR and chemisorption experiments, catalyst samples were rereduced *in situ* under 400 Torr H_2 for 2 h followed by evacuation for 2 h at 10^{-6} Torr at the reduction temperature. All gases used in pretreatment and adsorption experiments were ultrahigh purity grade and were further purified to remove H_2O and O_2.

CO/H_2 reactions were carried out in a tubular stainless-steel reactor. The reaction temperature was controlled by a thermocouple inserted into the catalyst bed. Prereduced catalyst (0.250 g) was heated in a hydrogen stream of 3.6 liters/h at 2 K/min to 673 K and was held at 673 K for 2 h before cooling to reaction temperature. The reaction was carried out at atmospheric pressure and 523–613 K using a 1 : 1 mixture of H_2/CO flowing at 2.4 liters/h. CO conversion was lower than 3% even at the highest temperature. After 5 min of reaction, a sample of the effluent gas was analyzed online. Details of the reaction system and product analysis are given elsewhere (*15*).

X-ray diffraction line broadening measurements were made in a General Electric XRD-5 spectrometer using Cu*Kα* radiation. Particle sizes greater than about 4 nm may be detected in these measurements.

RESULTS

A. Chemisorption Results

Table 2 gives results from volumetric measurements of H_2 and CO chemisorption on all catalysts. For catalysts prepared with the wide-pore SiO_2, the presence of the alkali species had no effect on the uptake of H_2 and only a slight effect on CO. Crystallite sizes measured from the H_2 uptakes were about 2 nm for both the unpromoted and promoted samples. X-ray diffraction line broadening measurements confirmed that crystallite sizes for all three catalysts were less than 4 nm.

The unpromoted Rh/SiO_2 catalyst exhibited a much larger crystallite size when prepared with the nonporous SiO_2 than with the wide-pore SiO_2. This was confirmed by X-ray line broadening measurements, which indicated an even larger average crystallite size of 12.5 nm for the unpromoted Rh supported on the nonporous SiO_2. The fact that hydrogen chemisorption measurements appear to overestimate the number of Rh sites suggests that spillover of hydrogen from metal sites to the support may have occurred.

TABLE 2

CO and H_2 Chemisorption Results

Catalyst[a]	H_2 uptake (μmol/g)[b]	CO uptake (μmol/g)[b]	Crystallite size (nm)[c]	CO/H[d]
I-1 : O-P	67	136	2.0[e]	1.01
SI-2 : 1-P	71	115	1.9[e]	0.81
SI-1 : 5-P	73	130	1.8[e]	0.89
I-1 : O-N	23	33	5.8[f]	0.72
CI-2 : 1-N	140	230	1.0[e]	0.82
CI-1 : 5-N	131	44	1.0[e]	0.17
SI-1 : 5-N	16	13	8.4[f]	0.41

[a] See text and Table 1 for explanation of catalyst designations.

[b] Taken from the total adsorption isotherm, rounded to the nearest micromole per gram.

[c] Based on total H_2 uptake.

[d] Atomic ratio.

[e] Crystallite size by X-ray line broadening <4.0 nm.

[f] Crystallite size by X-ray line broadening = 12.5 nm.

Hydrogen uptake *increased* significantly upon coimpregnation of the nonporous SiO_2 with the rhodium and alkali salts. The two catalysts promoted with different levels of K both exhibited crystallite sizes determined from the H_2 uptakes of about 1 nm, much smaller than for the unpromoted catalyst. The absence of a peak in the X-ray line broadening measurements indicated that the average crystallite sizes were below 4 nm.

While the H_2 uptakes for the Rh : K = 2 : 1 and Rh : K = 1 : 5 coimpregnated catalysts were very similar, there was a significant difference in their CO uptakes. The Rh : K = 2 : 1 sample appeared to adsorb a normal amount of CO, giving a CO/H ratio similar to those found for the 2 : 1 and 1 : 5 promoted catalysts in the wide-pore SiO_2

series. The 1 : 5 sample in this nonporous SiO$_2$ series, however, exhibited a significant suppression of CO adsorption, giving a CO/H ratio of only 0.17, a fivefold decrease in CO uptake.

A decrease in H$_2$ uptake was observed for the sequentially impregnated Rh : K = 1 : 5 nonporous SiO$_2$ catalyst compared to the unpromoted catalyst, giving a crystallite size of about 8.5 nm. These two catalysts came from the same reduced Rh/SiO$_2$ batch, the only difference being that the promoted catalyst went through a second impregnation with the alkali salt after reduction of the Rh salt. X-ray diffraction line broadening indicated that the crystallite size of this Rh : K = 1 : 5 sample was identical to that of the unpromoted catalyst with the same SiO$_2$ support. This suggests that the addition of K after reduction of the Rh/SiO$_2$ resulted in suppression of hydrogen adsorption on some sites. The crystallite size given by the X-ray measurement was still, however, much larger than that indicated by the H$_2$ chemisorption measurement.

CO adsorption was suppressed about twice as much as H$_2$ adsorption on this sequentially impregnated Rh/SiO$_2$. As a result, the CO/H ratio was about half as large for this catalyst compared to the unpromoted sample of the nonporous Rh/SiO$_2$.

B. Infrared Spectroscopic Results

IR spectra for CO adsorption on Rh supported on the widepore SiO$_2$ are shown in Fig. 1. The spectrum in Fig. 1A reveals features previously reported (*16–21*) for CO on Rh: two peaks at 2096 and 2032 cm^{-1} indicating the presence of the dicarbonyl species thought to adsorb on isolated Rh$^+$ sites; and linear and bridge CO with peaks at 2072 and 1880 cm^{-1}, respectively. The ratio of linear CO to the dicarbonyl species was greater than it was for Rh/Al$_2$O$_3$ (*6*), in agreement with literature results (*20*).

The effect of the addition of alkali on the adsorption of CO on this catalyst is shown in Figs. 1B and 1C. The only CO species affected by the presence of the alkali was the dicarbonyl. As the amount of alkali was increased, the dicarbonyl peaks decreased. The dicarbonyl was barely visible at Rh : K = 1 : 5. No shift in wavenumber was observed in either the linear or bridge CO as the level of alkali increased. These results agree very well with those found in our previous study for Rh/Al$_2$O$_3$ (*6*) in which no wavenumber shift with increasing alkali promotion level was observed.

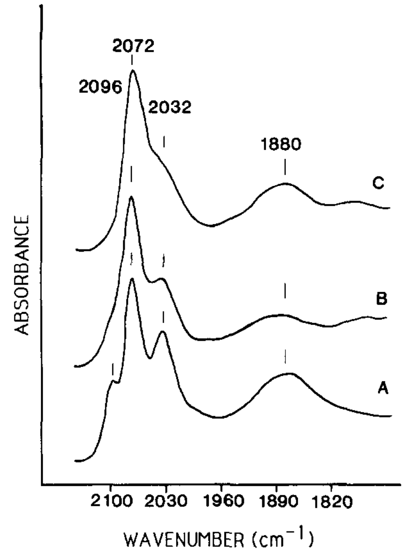

FIG. 1. IR spectra of CO adsorption on Rh/SiO$_2$ catalysts prepared from wide-pore SiO$_2$ (see Table 1 for explanation of catalyst designations). (A) Catalyst I-1 : 0-P; (B) catalyst SI-2 : 1-P; (C) catalyst SI-1 : 5-P.

The small decrease in the amount of CO adsorbed on the promoted samples from the chemisorption results in Table 2 may be compared with the decrease in the amount of the dicarbonyl species observed by IR. The disappearance of the dicarbonyl species appeared to coincide with a decrease in the CO uptake of 10–20%.

IR spectra for CO adsorption on Rh catalysts prepared with the nonporous SiO$_2$ are shown in Fig. 2. The spectrum for the unpromoted Rh/SiO$_2$ shown in Fig. 2A differs from that of the unpromoted sample from

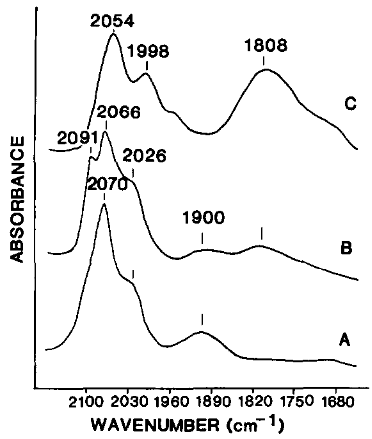

FIG. 2. IR spectra of CO adsorption on Rh/SiO_2 catalysts prepared from nonporous SiO_2 (see Table 1 for explanation of catalyst designations). (A) Catalyst I-1 : 0-N; (B) catalyst CI-2 : 1-N; (C) catalyst CI-1 : 5-N.

Fig. 1A in that the dicarbonyl peaks are substantially less prominent.

The spectra in Figs. 2B and 2C for CO adsorption on K-promoted catalysts prepared by coimpregnation of the Rh and K salts show some important changes from the unpromoted case. For the intermediate promotion level of Rh : K = 2 : 1, the dicarbonyl species actually showed an *increase* in intensity compared to the unpromoted catalyst, contrary to the previous results for both Rh/Al_2O_3 and Rh/SiO_2 (wide pore). The bridge CO peak decreased in intensity concomitant with the appearance of the second very weak peak near 1800 cm^{-1}. The wavenumber for linear CO decreased slightly.

More significant changes occurred at the high promotion level of Rh : K = 1 : 5, as can be seen in the spectrum of Fig. 2C. The dicarbonyl species disappeared and a new peak near 2000 cm^{-1} was observed. The bridge CO peak near 1900 cm^{-1} disappeared and the small band near 1800 cm^{-1} increased sharply in intensity. The linear CO peak continued to decrease in frequency.

The spectrum for CO adsorption on the nonporous SiO_2 Rh : K = 1 : 5 catalyst prepared by sequential impregnation is shown in Fig. 3, along with the spectra of the two other highly promoted Rh : K = 1 : 5 samples reproduced from Figs. 1C and 2C. The effect of the alkali species on CO adsorption was significant and was different for this catalyst than for the others previously discussed. The overall intensity of the CO spectrum was much less on this catalyst than on the others. The peaks for the dicarbonyl species were absent from the spectrum. The linear CO peak decreased in relative intensity and also shifted downward in wavenumber compared to the unpromoted catalyst. The bridge CO peak did not shift in frequency compared to the unpromoted catalyst. The most striking feature of this spectrum, however, was in the appearance of a new band at a wavenumber quite low for the CO stretching region, about 1680 cm^{-1}. This band was not present in the CO spectrum of any of the other catalysts investigated, nor was it present on the blank SiO_2.

Bands in the region of this new low frequency peak may be attributed to species other than adsorbed CO, such as carbonates, formates, or acetates. Adsorption of CO_2 in the absence of CO on this catalyst produced the spectra shown in Fig. 4. The

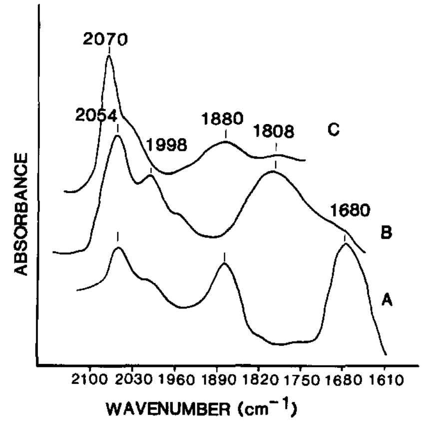

FIG. 3. Comparison of IR spectra for different catalysts with alkali loading of Rh : K = 1 : 5 (see Table 1 for explanation of catalyst designations). (A) Catalyst SI-1 : 5-N; (B) catalyst CI-1 : 5-N; (C) catalyst SI-1 : 5-P.

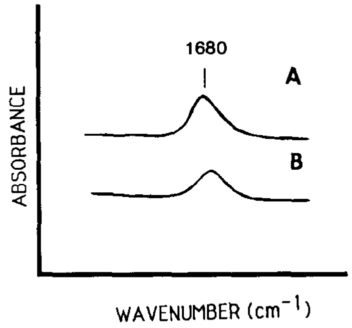

FIG. 4. IR spectra of CO$_2$ adsorption on the Rh/SiO$_2$ catalyst with Rh : K = 1 : 5 shown in Fig. 3A (A) with 5 Torr CO$_2$; (B) catalyst in A after 30-min evacuation.

only peak observed was this same low frequency band. After a 30-min evacuation of the cell, the band shifted to a slightly lower wavenumber but did not disappear.

C. *CO/H$_2$ Reaction Studies*

Results from CO/H$_2$ reactions over the unpromoted and the Rh : K = 1 : 5 catalysts are shown in Table 3. The activity of all of the catalysts studied was much lower than is found for Rh on supports other than SiO$_2$ (*5*). Oxygenated products were not observed although they constitute a large fraction of the products formed on Rh/SiO$_2$ when higher pressures are used (*5*). CO conversion and CO turnover frequency (TOF) varied over an order of magnitude between unpromoted and promoted samples. The TOFs for unpromoted Rh on the two different types of SiO$_2$ were identical, but the products formed from CO differed greatly on these two catalysts. The catalyst prepared with the nonporous SiO$_2$ produced more higher hydrocarbons and more olefinic products. It is useful to recall that this catalyst exhibited an average Rh crystallite size much greater than the other unpromoted Rh/SiO$_2$ (widepore).

The three different highly promoted Rh/SiO$_2$ catalysts all produced less higher hydrocarbons and less olefinic products than did the unpromoted catalysts. The Rh : K = 1 : 5 catalyst prepared with the wide-pore SiO$_2$ showed the least difference from the unpromoted case. This agrees well with IR and chemisorption results which revealed only slight differences in the adsorptive properties of promoted catalysts prepared from the wide-pore SiO$_2$.

The coimpregnated Rh : K = 1 : 5 catalyst prepared from the nonporous SiO$_2$ showed a significant *increase* in selectivity toward methane and very low selectivity for olefin formation compared to the unpromoted case. The catalyst prepared by sequential impregnation on this same SiO$_2$ showed the same trends but with a less dramatic shift in products.

Apparent activation energies for these catalysts were all in the range of 27–33 kcal/g · mol with the exception of the sequentially impregnated Rh : K = 1 : 5 sample prepared from the nonporous SiO$_2$. This catalyst exhibited a drastic decrease in apparent activation energy to 12.6 kcal/g · mol.

DISCUSSION

A. *IR and Chemisorption Studies*

Wide-pore SiO$_2$. The results shown in Fig. 1 and Table 2 indicate that the addition

TABLE 3

CO/H$_2$ Reaction Results

	Catalyst[a]				
	I-1 : 0-P	SI-1 : 5-P	I-1 : 0-N	SI-1 : 5-N	CI-1 : 5-N
% CO conv.	0.99	0.03	0.38	0.02	0.06
TOF (×10^3) (s^{-1})[b]	4.10	0.10	4.52	0.36	0.13
E_{app} (kcal/mol)	30.9	28.7	27.1	12.6	32.9
Selectivity (wt%)					
C1	65.2	67.2	44.1	52.9	87.6
C2	14.1	20.9	13.9	32.7	9.6
C3	13.2	9.0	20.6	14.4	2.9
C4	5.6	3.0	9.8	0.0	0.0
C5	2.0	0.0	5.9	0.0	0.0
C6$^+$[c]	0.0	0.0	5.8	0.0	0.0
C3$^-$/C3[d]	1.3	0.3	11.9	0.7	0.0

[a] Catalyst descriptions are given in Table 1.
[b] Turnover frequency for CO.
[c] Products with six or more carbon atoms.
[d] Ratio of propylene to propane.

of alkali even in large concentrations had very minor effects on the adsorptive properties of Rh supported on the wide-pore SiO_2. This agrees very well with our previously reported results for the Rh–Cs/Al_2O_3 system (*6*). It was suggested that the alkali preferentially partitioned to the support and hence very little alkali–Rh interaction was observed. It appears that this same effect occurred for Rh supported on the wide-pore SiO_2. The only observable effects of the presence of the alkali on the adsorptive properties were the decrease in the dicarbonyl species observed by IR and the small decrease in CO uptake measured volumetrically. Both of these results support the suggestion that the only surface sites with which the alkali interacts strongly are the isolated Rh^+ sites atomically dispersed on the support.

Recent studies of the adsorption of CO on small supported Rh crystallites have suggested that CO itself may act to alter the metal surface structure. Extended X-ray absorption fine structure (EXAFS) (*22*) and radial electron distribution (RED) (*23*) measurements have implied that small Rh crystallites may disintegrate upon contact with CO, forming $Rh(CO)_2$ entities dispersed over the support. In light of these studies, it might be suggested that the effect of alkali on Rh supported on the wide-pore SiO_2 is to inhibit the action of CO in redispersing Rh rather than to block sites for dicarbonyl formation. The lack of observable effects of the alkali species on the linear and bridge CO still supports the suggestion that the alkali partitioned to the support. Perhaps the mobility of $Rh(CO)_2$ entities across the support is inhibited with alkali present, forcing the $Rh(CO)_2$ species to reagglomerate into Rh crystallites. Since our measurements of H_2 uptake were made only before the catalysts were exposed to CO, it is not possible to determine whether this suggested redispersion occurred or not.

Alkali promotion of Rh supported on the wide-pore SiO_2 appeared to produce an alkali-covered support surface which either inhibited the mobility of $Rh(CO)_2$ or blocked the adsorption of CO on isolated Rh^+ sites already present on the support. No geometric or electronic effects of the alkali species on adsorption on reduced Rh crystallites were observed.

Nonporous SiO_2. When the nonporous SiO_2 was used as a support, the characteristics of both the unpromoted and alkali-promoted catalysts were significantly different than those prepared with the wide-pore SiO_2. The unpromoted Rh on the nonporous support showed substantially less dicarbonyl species than did Rh on the wide pore support, as can be seen by comparing Figs. 1A and 2A. H_2 uptakes and X-ray diffraction confirmed that the crystallite size of the catalyst prepared using the nonporous SiO_2 was significantly larger. Hence, the nonporous SiO_2 catalyst either initially had few isolated Rh^+ sites for dicarbonyl formation because of its larger average crystallite size, or its large crystallite size prevented the formation of these sites upon contact with CO (*22, 23*).

The significant difference between the crystallite size determined by X-ray diffraction and by H_2 chemisorption indicates that spillover of hydrogen from the Rh to sites on the support may occur. This has been suggested previously for supported Rh (*24–26*), and suggests that H_2 adsorption measurements may not be an accurate method of determining Rh crystallite sizes.

When the alkali promoter was coimpregnated at a concentration of Rh : K = 2 : 1 on the nonporous SiO_2, several intriguing observations were made. The dicarbonyl peaks actually *increased*, contrary to the trend observed previously of decreasing dicarbonyl peaks with increasing alkali content. The H_2 uptake increased tremendously, and the crystallite size measured by X-ray decreased to below the 4-nm detection limit. It appears that the presence of a small amount of alkali coimpregnated with the Rh/SiO_2 actually helped to increase the dispersion of the Rh. With this increase in dispersion came an increase in H_2 uptake and an increase in the CO IR features common to smaller crystallites of Rh.

An increase in the dispersion of supported transition metals with the addition of alkali species has been observed before (*12*, *27*). The alkali may act to keep the Rh from sintering, which may be especially important for Rh dispersed on the small SiO_2 particles of the nonporous support. This suggests a much more intimate alkali–Rh interaction on coimpregnated, nonporous SiO_2 catalysts than was observed for the sequentially impregnated, wide-pore SiO_2 catalysts.

The linear CO peak for the Rh : K = 2 : 1 sample decreased slightly in frequency. The CO/H ratio was close to that of the unpromoted sample. A downward shift in the linear CO frequency might result if the adsorbed CO dipoles are not able to interact as they do in the absence of the intruding alkali surface species (*28*, *29*). The decreased bridge CO intensity supports a geometric intrusion of the alkali species to disrupt bridge CO adsorption without blocking Rh sites for hydrogen adsorption. The weak band appearing at lower frequency in the bridge CO region may indicate either CO adsorption on a different site or the onset of an electronic effect of the alkali species on some of the adsorbed CO.

When the K promotion level for the coimpregnated catalyst was increased to Rh : K = 1 : 5, more significant changes were observed in the adsorption of CO. The continued downshift in linear CO frequency was coupled with the growth of the weak feature near 1800 cm^{-1} to an intense peak. This sample also exhibited strong suppression of CO adsorption, suggesting that a Rh site-blocking effect occurred for CO adsorption at high alkali concentrations. A decrease in CO adsorption caused by a substantial blocking of Rh sites might also cause a decrease in the dipole–dipole interactions of CO molecules by breaking up ensembles of neighboring adsorption sites. It follows that the bridge CO region might be affected more by this site blockage since the required ensemble size is greater for bridge than for linear bonding. The coverage and the dipole–dipole coupling of bridge CO species might be decreased to a greater extent than for linear CO. However, this proposed site blocking would appear to affect only CO and not H_2 adsorption. In addition, a geometric argument based on the breakup of dipole–dipole interactions causing a downward frequency shift of bridge CO cannot explain the dramatic intensity increase of the low frequency peak.

A change in the adsorption site for CO to a site with a different extinction coefficient might cause a change in intensity unrelated to a change in concentration of adsorbed CO molecules. Single crystal (*9*) studies on K-promoted Rh(111) have noted dramatic increases in intensity of peaks in the bridge CO region concomitant with a change in the site-filling sequence from linear to bridge CO. The fivefold suppression of CO adsorption in the absence of H_2 suppression suggests that if a change in the CO adsorption site occurred upon K promotion, the new site involved threefold or even more highly coordinated CO–metal species. Since more highly coordinated CO should exhibit a lower CO stretching frequency, perhaps this might explain both the frequency and intensity changes in the spectrum of adsorbed CO on coimpregnated Rh/SiO_2 catalysts.

Intuitive arguments concerning the dilution of an adsorbent surface with another species would suggest, however, that adsorption sites requiring a larger ensemble of surface atoms would *decrease* rather than increase as the diluting species increases in concentration. An electronic effect might instead be considered in which the Rh electron density is increased in the presence of the alkali species, causing downward shifts in frequency of CO stretching vibrations. The peak at 1808 cm^{-1} may indeed be the same bridge CO species formerly found near 1900 cm^{-1} in the absence of alkali. It remains, however, to explain the sharp increase in intensity of the bridge CO peak with alkali promotion and how it might be related to this electronic effect. It has been observed (*30*) for transition metal–CN complexes (which may be considered as analogous to metal–CO bonds) that the intensity of the C–N band may increase as the number of *d*-electrons involved in the π-bonding increases. The intensity of the vibration may be used as a measure of the extent of metal–cyanide π-bonding. If the electronic interaction of the alkali species with the metal results in an increase in the electron density of the metal atoms as suggested (*7*), this could be tantamount to an increase in the number of *d*-electrons involved in the metal–carbon monoxide π-bonding. Thus both the frequency downshift and the intensity increase in the bridge CO peak might be attributed to the electronic interaction of the alkali species with the Rh surface atoms.

In addition to the changes in the linear and bridge CO peaks described above, a new peak appeared near 2000 cm^{-1} in the CO IR spectrum for the Rh : K = 1 : 5 sample. This peak cannot be attributed to the asymmetric stretch of the dicarbonyl species shifted to lower frequency since the symmetric stretch is missing, and because previous studies (*17–21*) have noted that the stretching frequency for this species does not exhibit strong shifts with changes in its environment. Peaks in this region have been observed before for supported Rh catalysts which have been exposed to oxygen (*31*). These peaks have been assigned to either linear or bridge CO on oxidized Rh sites. Since the alkali species on these catalysts was probably present as either an oxide or a hydroxide (*12*), it may be suggested that the peak near 2000 cm^{-1} corresponds to CO adsorbed on selected Rh sites which interact with the anionic portion of the alkali species. However, it is difficult to assign this peak on such little evidence. It is important to note that a peak in this region has been observed before for alkali-promoted $\mathrm{Rh/Al_2O_3}$ (*6*).

When sequential impregnation was used to prepare the Rh : K = 1 : 5 sample on the nonporous $\mathrm{SiO_2}$, the effects were completely different than when the samples were coimpregnated. The dispersing effect of the alkali species was not observed when the alkali was added after the initial decomposition/reduction of the Rh salt. It appears that once decomposition of the $\mathrm{Rh(NO_3)_3}$ salt to form Rh crystallites has occurred in the absence of an alkali salt, it is no longer possible to break up these crystallites by addition of an alkali salt.

Both hydrogen and carbon monoxide adsorption were suppressed on the sequentially impregnated Rh : K = 1 : 5 sample, but CO was suppressed about twice as much. The overall weaker intensity of the IR spectrum of CO also suggests that adsorption of CO on this catalyst was less. The absence of the dicarbonyl species and the larger crystallite size of this sample again suggested the absence of isolated $\mathrm{Rh^+}$ sites. The bridge CO species appeared at precisely the same wavenumber as for the unpromoted catalyst, indicating the absence of both electronic and geometric effects of the types discussed previously for the coimpregnated samples. An intriguing new peak at a very low wavenumber for the bridge CO region suggests that a different type of interaction or adsorption site, or even a different adsorbed species, might be present on this promoted sample. Adsorption of $\mathrm{CO_2}$ on this Rh : K = 1 : 5 sequentially impregnated sample produced this same low-frequency peak. The absence of other peaks makes it difficult to assign this peak to a carbonate species. However, there have been several suggestions from both supported metal (*1, 32–37*) and single crystal (*38–46*) studies to explain anomalous low-frequency peaks in vibrational spectra of adsorbed CO. Predominantly short-range interactions between adsorbed CO and alkali or other species have been invoked in these explanations.

Ichikawa and co-workers (*1*) recently found a CO peak at very low wavenumber for Rh/SiO$_2$ catalysts promoted with Mn and Ti oxides. They attributed this peak to the CO stretching vibration for CO adsorbed in a tilted fashion on Rh with the oxygen interacting directly with moieties of the metal–oxide promoters adjacent to the Rh crystallite. Others have suggested similar assignments for low frequency CO IR peaks based on analogies with organometallic complexes (*32*). Interactions between the oxygen of the adsorbed CO and titania suboxides has been suggested for supported Pt (*33*), Ni (*34, 35*), and Fe (*36*). In another study Lewis acid sites on Al$_2$O$_3$ were thought to interact with the oxygen of CO adsorbed on Ru catalysts (*37*).

Other studies on single crystal surfaces (*38–42*) also point to a change in orientation of the CO molecule adsorbed on surfaces containing alkali species. In studies of coadsorbed K and CO on Ru(001), both Hoffmann and de Paola (*38*) and Netzer *et al.* (*39*) suggested a change in the bonding configuration of CO from an upright to an inclined or side-on position in a strong localized interaction with coadsorbed K. Further work on Ru(001) and Cu(001) (*40, 41*) revealed changes in the symmetry of adsorbed CO in the presence of K. Increased backbonding involving the $2\pi^*$ molecular orbitals of CO is accompanied by direct interaction of the 1π molecular orbitals of CO with K. This interaction was postulated to account for the large frequency shifts in vibrational spectra of coadsorbed CO and K that could not be accounted for simply by invoking the through-metal interaction that results in increased occupancy of the 2π orbitals. This type of direct CO–K interaction was suggested by Lackey *et al.* (*42*) to cause the formation of polymeric K–CO adsorbate complexes. Uram *et al.* (*43*) also postulated the formation of K–CO surface complexes on Ni(111) manifested by a high temperature desorption state. This state was characterized by the simultaneous desorption of CO and K and was found only at high K coverages. It was suggested that this desorption state might be due to a K–CO complex similar to potassium deltate, K$_2$(CO)$_3$ (*44*). In other studies, no changes were found in the orientation of CO on metal surfaces with alkali atoms coadsorbed (*45, 46*) although rehybridization of the CO molecular orbitals has been suggested to occur because of the metal–K interaction (*45*).

It is clear from the studies described above that alkali species in the vicinity of adsorbed CO can have a strong influence on how CO interacts with the surface, perhaps by a through-metal electronic interaction as well as by a direct interaction between the alkali species and the CO molecule. While CO adsorption on the coimpregnated Rh : K = 1 : 5 catalyst on nonporous SiO$_2$ appeared to exhibit interactions best described by the through-metal electronic model, the sequentially promoted catalyst prepared from the same SiO$_2$ demonstrated adsorptive characteristics similar to systems in which a direct alkali–CO interaction is present. It appears that some of the Rh–K sites on the sequentially impregnated Rh : K = 1 : 5 sample are capable of forming K–CO complexes from either adsorbed CO or from adsorption and disproportionation of CO$_2$.

Why this type of CO–alkali interaction should occur for the sequentially impregnated but not for the coimpregnated catalysts is an intriguing question. This sequential impregnation preparation procedure did not result in a metal surface completely covered with alkali even at this extremely high alkali species concentration, since both IR and chemisorption results showed that adsorption was suppressed but not eliminated. The alkali species also was unable to intrude between Rh atoms and disperse the metal crystallites. The alkali species itself must agglomerate into particles which interact with certain metal sites, perhaps at the metal–support interface. When CO adsorbs on these metal sites, an agglomerated alkali particle nearby participates in some type of interaction which involves tilting of the CO such that the oxygen end of the molecule interacts strongly with the K species, even forming a Rh–CO–K complex. The interaction is strong enough that CO_2 may disproportionate on these sites to form this complex. This interaction must be localized in nature because the normal bridge CO frequency is unaffected by the presence of these alkali particles.

The state and location of the alkali species differ greatly with the method of preparation of catalysts prepared with the nonporous SiO_2. Sequential impregnation did not afford the intimate Rh–alkali contact which occurred when the two salts were decomposed together. In the case of the coimpregnated catalyst, the alkali species appears not to agglomerate into particles but to wet the surface of the SiO_2 particles while it helps to keep the Rh from sintering into large crystallites. It seems that this intimate contact is necessary to produce the through-metal type of electronic interaction suggested earlier for the coimpregnated catalysts. It also appears that agglomeration of the alkali species in close proximity to some metal sites causes a localized interaction in the form of a Rh–CO–K complex.

B. CO/H_2 Reaction Studies

Although the activity of both unpromoted and promoted catalysts was quite low, some important observations could be made from these data. Comparison of the products formed from the two unpromoted catalysts prepared from different types of SiO_2 suggests a crystallite size effect in which substantially more higher hydrocarbons and more olefinic products are produced from the sample with the larger crystallite size.

The activity fell by at least an order of magnitude for all promoted catalysts compared to the two unpromoted catalysts. The sequentially impregnated catalyst prepared from the wide-pore SiO_2 exhibited the smallest change in product selectivity upon promotion with the alkali species. This catalyst also exhibited only slight changes in adsorptive properties for CO and H_2 compared to the unpromoted catalyst. It is intriguing that the only observable effect of the presence of the alkali species is a drastic decrease in activity with no visible changes in other reaction parameters or adsorptive properties. This seems to indicate that the sites which turn over CO on the surface are not the sites that are counted by quantitative chemisorption measurements or the sites which are observed by IR spectroscopy of adsorbed CO. These results support recent studies (*47–50*) suggesting that only a small fraction of metal surface sites may actually participate in CO/H_2 reactions. Since only the adsorptive properties averaged over all surface sites, catalytically active and catalytically unimportant, are measured by IR and chemisorption experiments, neither technique provides much information about the reactivity of surfaces on which a small minority of sites are responsible for most of the reactivity.

The substantial shifts in product selectivity exhibited by the coimpregnated catalyst prepared with the nonporous SiO_2 may be correlated with the strong suppression of CO adsorption on this catalyst. At the extremely low CO conversion rate found for this catalyst, the small amount of CO adsorbed on a hydrogen-rich surface converts almost exclusively to methane.

The most striking feature of the reaction results on the sequentially impregnated catalyst prepared on the nonporous SiO_2 was its sharply lower apparent activation energy. The apparent activation energy for CO conversion represents a combination of different terms including the intrinsic activation energy and the heat of adsorption of CO. Since the rate of CO conversion on this catalyst was extremely low, a small shift in one of these terms might result in a dramatic change in the apparent activation energy. It can be recalled that this catalyst exhibited the unusual low frequency CO adsorption feature in the IR spectrum that was attributed to a strong Rh–CO–K interaction. The CO molecules involved in this interaction may also be involved in hydrogenation, and they may have a much higher heat of adsorption than CO adsorbed in the normal linear and bridge modes. This difference may be sufficient to produce the observed alteration in activation energy.

Neither of the promoted catalysts prepared with the nonporous SiO_2 produced reaction results typical of the effects found for alkali-promoted catalysts in other studies (*5*). Dramatic changes in adsorptive properties of these catalysts upon promotion with alkali were not matched by dramatic changes in product selectivity. Again, the *activity* of the promoted catalysts decreased significantly but this decrease did not appear to be related in any straightforward way to the changes observed in adsorptive properties.

The reaction conditions used did not provide the most sensitive probe of the effects of alkali promotion, since both the extremely low activity and the inability to produce oxygenated products at low pressure restricted the observations which could be made. In fact, the meager activity of these catalysts may have resulted in a larger relative contribution from "unusual" sites than is found for systems which display higher overall activity. It is interesting that CO/H_2 reactions can proceed at all on catalysts so heavily promoted with alkali species.

CONCLUSIONS

The effects of alkali promotion on the adsorptive and reactive properties of Rh/SiO_2 catalysts were investigated as a function of preparation parameters including the type of SiO_2 support and the method of addition of the alkali precursor salt. The effects observed were found to depend highly on these parameters.

Alkali species on a wide-pore SiO_2 support tended to partition preferentially to the support, and little interaction with the Rh was observed. Coimpregnation of the alkali and metal salts on a nonporous SiO_2 support helped increase the dispersion of the Rh and resulted in a through-metal electronic interaction between the alkali species and the metal. Sequential impregnation of the nonporous SiO_2, which involved reduction of the Rh precursor prior to addition of the alkali species, resulted in a different effect. This was attributed to a localized interaction between the oxygen of an adsorbed CO and the alkali species itself.

The nature and location of the alkali species on the catalyst surface were suggested to be important parameters in determining the type of effect that addition of alkali promoters can have on the adsorptive properties of the catalyst. When alkali and Rh salts were coimpregnated and decomposed together, the alkali appeared to wet the surface of the support. Alkali salts added after the reduction of the Rh precursor seemed to agglomerate in particles.

While the CO conversion rate decreased substantially on all of the promoted catalysts compared to the unpromoted catalysts, the product selectivities showed less dramatic changes. The product distribution was very similar for the promoted and unpromoted catalysts prepared with the wide-pore SiO_2. The decrease in CO adsorption on the coimpregnated catalyst prepared with the nonporous SiO_2 was matched by an increase in selectivity toward methane. The sequentially impregnated catalyst from the same SiO_2 exhibited an unusually low apparent activation energy for CO conversion which was suggested to be related to the unusually low frequency CO peak observed by IR spectroscopy.

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