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The Nature of Rh–CO Interactions on SAPO-5-Supported Rh

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The adsorption of CO on Rh/SAPO-5 showed the formation of a high-frequency dicarbonyl species that depended on time and temperature of adsorption as well as on the presence of oxygen. Other adsorbates including H_2, water, and surface carbon inhibited the formation of this species, which was held tightly to the SAPO-5 support but was also shown to be labile for CO exchange. This dicarbonyl species was proposed to be due to a $Rh/(CO)_2$ cationic species which may serve as the neutralizing cation in the ion-exchangeable SAPO-5 structure. This study combined with observations made in other work helped to construct a more coherent picture of the nature of the Rh–CO interaction on molecular sieve supports.

INTRODUCTION

The adsorption of CO on supported Rh catalysts has been a subject of intense interest through the three decades since Yang and Garland (*1*) proposed several structures for Rh–CO surface species. In that classic work they suggested the existence of a gem-dicarbonyl adsorbed species, $Rh(CO)_2$ (2095 and 2027 cm^{-1}), from comparison of the infrared spectrum of CO adsorbed on Rh/Al_2O_3 to that of the model compound rhodium carbonyl chloride, $Rh_2(CO)_4Cl_2$. This dicarbonyl was thought to form on highly dispersed or partially oxidized Rh sites. Several studies of CO adsorbed on Rh supported on different molecular sieves have detailed the existence of a second type of dicarbonyl species exhibiting a higher frequency IR doublet near 2115 and 2048 cm^{-1} (*2–5*). It has been suggested that the lower frequency doublet results from $Rh(CO)_2$ in which the Rh is bound to two support oxygen atoms, while for the high-frequency dicarbonyl species one of these oxygen atoms is replaced by a water molecule (*3*).

An important recent result was the finding that the formation of the gem-dicarbonyl is due to the corrosive chemisorption of CO. The adsorption of CO on small Rh crystallites *causes* the disintegration of these crystallites into isolated $Rh^+(CO)_2$ species interacting strongly with the support material. This idea was suggested earlier (*6, 7*) and was later convincingly demonstrated in EXAFS and radial electron distribution (RED) studies by Prins and co-workers (*8, 9*) and Gallezot and co-workers (*10*), respectively.

The use of CO as a probe molecule has become a routine method of characterization of supported metal crystallites. For studies of Rh-based catalysts, however, the corrosive chemisorption of CO brings into question the validity of a probe which in fact alters the nature of the surface it examines. The present study of CO adsorption on Rh/SAPO-5 was undertaken to learn more about the nature of dicarbonyl species and the conditions under which they may form. Results for this novel molecular sieve support are compared to those for SiO_2, Al_2O_3, and other molecular sieves

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both from our work and from the literature.

EXPERIMENTAL

The SAPO-5 support used in these studies was prepared and characterized as described elsewhere (*11–13*). The sample used in this study was a low-SiO_2 example of the 12-ring AlPO-5 structure which substitutes Si for P or two Si pairwise for an Al–P pair. The incorporation of Si produces an anionic material requiring neutralizing cations. The straight pore structure has no precise aluminosilicate analog although it resembles the mordenite structure. SAPO-5 has a fairly large pore diameter of 0.73 nm. Table 1 gives information about the chemical composition of this support.

The SAPO-5 was calcined in oxygen at 473 K for 2 h prior to preparing Rh-supported SAPO-5 by ion-exchange of $Rh(Cl)_3$ (*14*) to a weight loading of 1.6% (Galbraith laboratories and the University of Pittsburgh Applied Research Center (U-PARC) analytical laboratories). Several Rh catalysts were prepared on other supports for comparison. Rh/mordenite samples of nominal weight loading 1.5% were prepared using similar ion-exchange techniques with a Na-mordenite (Norton) support. A Rh/SiO_2 (Davison 952) catalyst was prepared by impregnation techniques described previously (*15*). All catalysts were reduced in flowing hydrogen for 16 h at 673 K after a temperature ramp of 0.5 K/min. Samples were stored in air until use.

TABLE 1

Properties of SAPO-5 and Rh/SAPO-5

Composition		Method
Si/Al	P/Al	
0.10	0.90	Bulk analysis
0.12	0.88	Microprobe
Pore volume:	0.18 ml/g	
Pore diameter:	0.73 nm	
Rh crystallite size:	1.2 nm (volumetric chemisorption 1–2 nm (TEM)	

Metal crystallite size and size distribution for Rh/SAPO-5 were obtained from transmission electron microscopy (Fig. 1), using a JEOL 100X microscope on ultramicrotome cuts of the SAPO-5 embedded in an epoxy resin. Metal dispersion was also measured by hydrogen chemisorption in a standard glass volumetric chemisorption system capable of 10^{-6} Torr. Prior to IR and chemisorption studies, samples were re-reduced at 673 K under 400 Torr hydrogen for 1 h followed by evacuation for 1 h at the same temperature.

Infrared spectroscopic measurements were performed with a Mattson Polaris FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and using 4-cm^{-1} resolution and coaddition of 400 scans. IR samples were prepared by pressing a self-supporting wafer of the Rh-SAPO-5 mixed with a small amount of SiO_2 (Davison 952) as a binder. An *in situ* cell allowed spectra to be recorded under different temperatures and gas-phase compositions. Samples were exposed to 10–50 Torr CO followed by evacuation to 1 Torr. Oxygen, hydrogen, carbon, and water were coadsorbed with CO in ambient temperature experiments. Oxygen and water were adsorbed at 10 Torr prior to CO adsorption in separate experiments. A hydrogen-covered surface was obtained after re-reduction by cooling the sample in the IR cell under hydrogen instead of evacuating it at high temperature. Surface carbon was produced by heating to 673 K under 50 Torr carbon monoxide.

RESULTS

The weight loading of Rh in the SAPO-5 structure was close to the maximum ion-exchange capability of this low-silica support. An average crystallite size of 1.2 nm was found by hydrogen chemisorption. Rhodium crystallites smaller than 1 nm, fitting in the SAPO-5 pores, were detected in

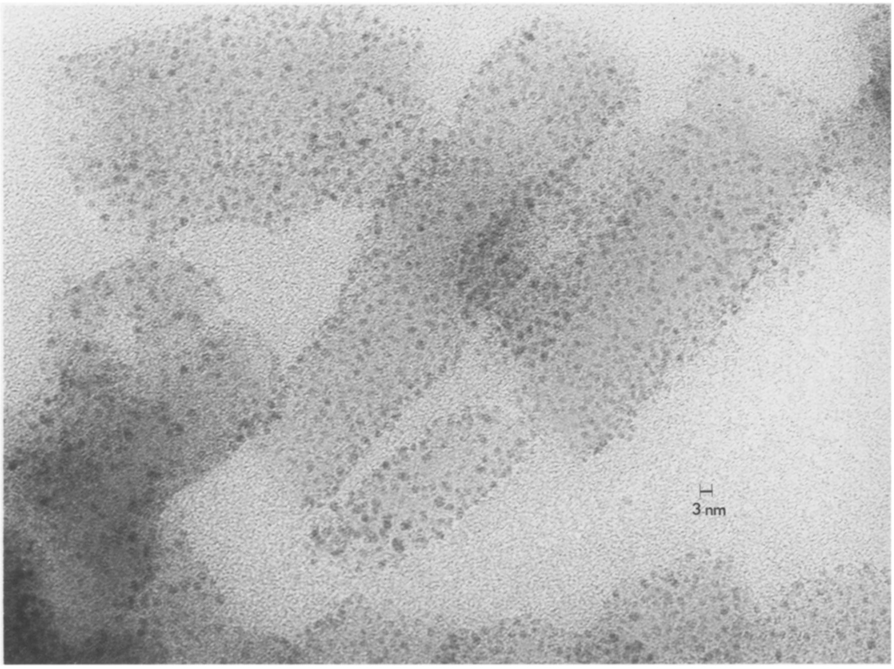

FIG. 1. Transmission electron micrograph of reduced Rh/SAPO-5 showing crystallite size distribution.

the ultramicrotome cut viewed by TEM (Fig. 1). However, a number of particles in the size range 1–1.5 nm were observed, appearing to be encapsulated in the SAPO-5 framework but larger than the pore diameter. This has been observed previously on zeolite-supported metal catalysts (*16, 17*). The metal particle growth implied the breaking of framework linkages around the metal particles.

IR spectra of 10 Torr of CO adsorbed on Rh/SAPO-5 at ambient temperature as a function of time are shown in Fig. 2. Immediately after adsorption, linear and bridge CO species dominated the spectrum, and only the breadth of the linear CO peak at 2062 cm^{-1} hinted at the presence of a doublet indicative of dicarbonyl species. With time, however, peaks at 2109 and 2044 cm^{-1} began to form in concert and became quite sharp over 48 h.

The effect of oxygen on the formation of this high-frequency doublet (HF) was similar to the effect of time (Fig. 3). Preadsorbed oxygen accelerated its formation significantly. When oxygen was added after CO adsorption, or when the sample underwent CO/O_2 cycles, the doublet was also enhanced, but the process required more time.

The formation of the doublet was dependent on the temperature of CO adsorption. Figure 4 shows that the formation of the doublet was more rapid at 473 K than at either ambient temperature or at 673 K. Heating under vacuum after CO adsorption at 673 K resulted in decreases in the intensity of the linear CO peak, but the high-frequency doublet persisted during heating under vacuum at 573 K, as shown in Fig. 5.

The effect of O_2 adsorbed on other supported Rh catalysts is shown in Fig. 6. Rh/SiO_2 exhibited a strong LF doublet, while a strong HF doublet was observed on Rh/mordenite. The mordenite-supported Rh also exhibited a new dominant peak near 2011 cm^{-1} which was enhanced in the presence of oxygen.

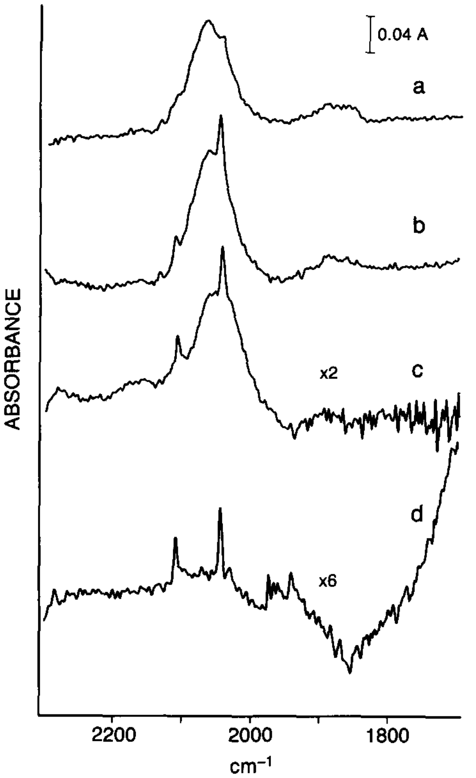

FIG. 2. IR spectra of 10 Torr CO on Rh/SAPO-5 as a function of time at ambient temperature (a) immediately after adsorption; (b) 16 h; (c) 116 h; (d) 408 h.

The effects of coadsorbates other than oxygen are shown in Fig. 7. The formation of the HF doublet appeared to be inhibited by hydrogen, carbon, and water vapor. Peaks for linear and bridge CO were unaffected in intensity or frequency by the presence of coadsorbates, and in fact all three appeared to inhibit it, as witnessed by the lack of strong peaks for the HF dicarbonyl even after 18–48 h.

^{12}CO–^{13}CO adsorption experiments were carried out to study rates of exchange of different adsorbed CO species on Rh/SAPO-5. Figure 8 reveals that for the high-frequency doublet, CO exchange was rapid and complete at ambient temperature within the time required to acquire a spectrum. CO adsorbed in the bridge CO form did not exchange at all within several hours after adsorption.

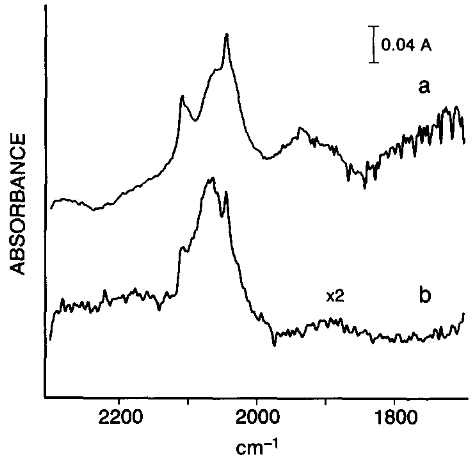

FIG. 3. Effect of oxygen on the CO IR spectra of Rh/SAPO-5 (a) 18 h after three CO/O$_2$ cycles; (b) preadsorption of 6 Torr O$_2$ followed by 10 Torr CO.

The angle between two CO molecules bound to the same Rh atom in a dicarbonyl species is related to the ratio of integrated intensities of the symmetric and asymmetric peaks by the equation (*18*)

$$(I_{\mathrm{sym}})/(I_{\mathrm{asym}}) = \cot^2 \theta/2.$$

This ratio of the intensity of the symmetric to the asymmetric peak in the dicar-

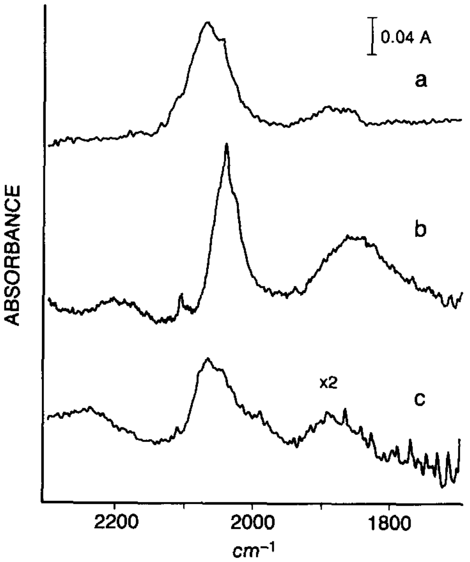

FIG. 4. Effect of the initial CO adsorption temperature of 10 Torr CO on the CO IR spectra of Rh/SAPO-5. (a) 298 K; (b) 473 K; (c) 673 K.

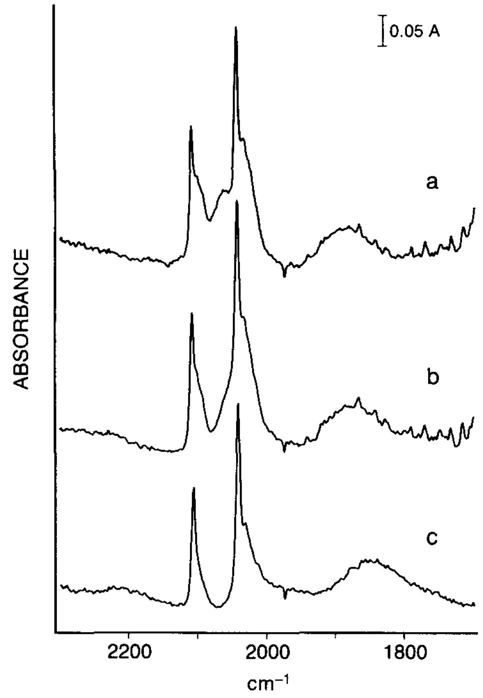

FIG. 5. Effect of high-temperature evacuation on the CO IR spectra of oxidized Rh/SAPO-5. (a) 298 K; (b) 373 K; (c) 573 K.

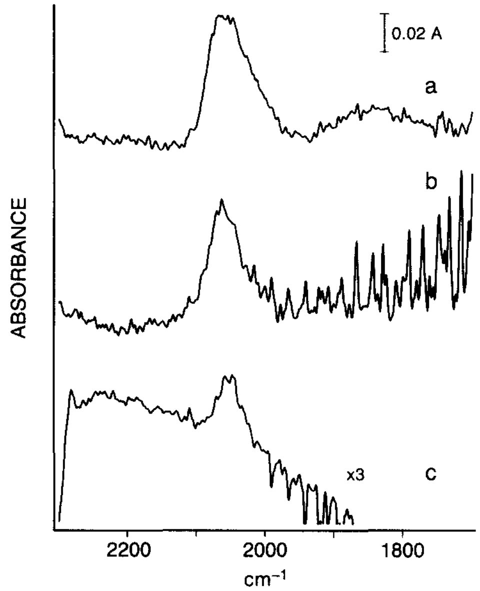

FIG. 7. Effect of the preadsorption of other adsorbates on the CO IR spectra of Rh/SAPO-5. Times in parentheses refer to time of CO adsorption at ambient temperature. (a) H_2 (20 h); (b) surface carbon (18 h); (c) H_2O (48 h).

bonyl species was found to be a function of the type of support. Table 2 lists these OC–Rh–CO angles for the catalysts used in this study as well as for some catalysts reported in other work. The Rh/SAPO-5 catalyst bears a closer resemblance to Rh supported on faujasite supports than to the Rh/mordenite catalyst of more similar support structure. SAPO-5 is similar to the faujasites in acidity but is closer to mordenite in structure, since mordenite has one-dimensional channels of diameter similar to SAPO-5 rather than supercages (although mordenite also contains 0.4-nm channels).

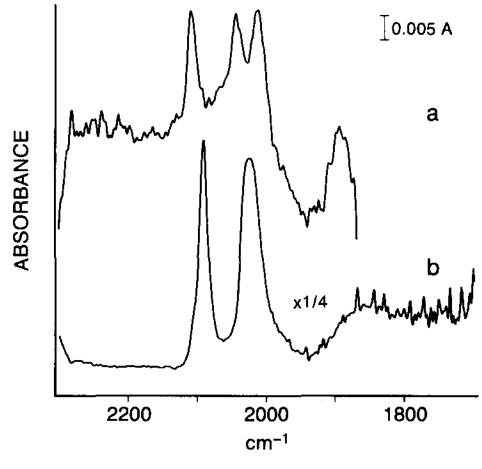

FIG. 6. Effect of oxygen on the CO IR spectra of other supported Rh catalysts. (a) Rh/mordenite (adsorption at 473 K), after 16 h; (b) Rh/SiO_2 (adsorption at 298 K), after 18 h.

DISCUSSION

IR spectra of CO adsorption on Rh/SAPO-5 agree well with published reports for CO adsorption on supported Rh, especially for Rh supported on molecular sieves (*2–5, 10*). The behavior of the high-frequency doublet in particular was followed under various conditions. While it has been suggested (*3*) that this doublet forms when one of the surface oxygen atoms bound to a $Rh(CO)_2$ species is replaced with a water molecule, our experiments showed no ef-

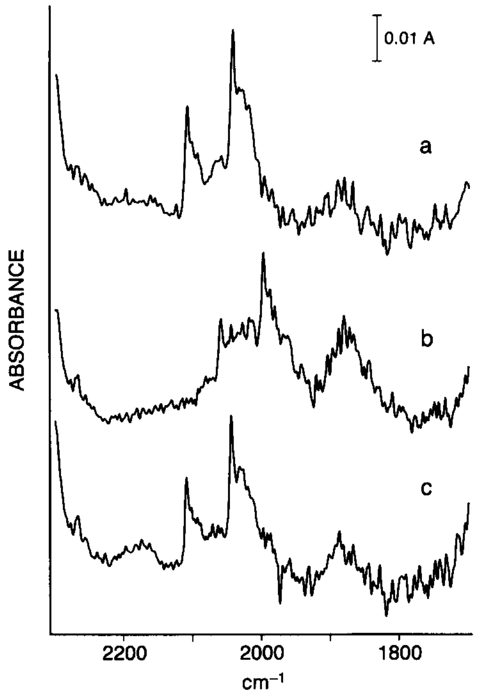

FIG. 8. Effect of ^{13}CO–^{12}CO exchange on the CO IR spectra of Rh/SAPO-5 catalysts. (a) ^{12}CO on oxidized sample; (b) ^{13}CO addition to the sample in spectrum a; (c) ^{12}CO re-exchange with the sample in spectrum b.

fect of the addition of water on the intensity of the HF dicarbonyl species. In fact, the only coadsorbate found to enhance this species was oxygen. This suggests that the formation of this dicarbonyl species is tied to an oxidation process or an oxide species.

One commonality to all of the published observations of the HF dicarbonyl species is that ion-exchangeable molecular sieves were used as supports and that the catalysts were prepared by ion-exchange of Rh into the structure. SAPO-5 is made up of PO_2^+, AlO_2^-, and SiO_2 groups. The incorporation of Si for P results in an anionic structure needing cations to neutralize its structure. This requirement was fulfilled by Rh^{3+} cations introduced during the ion-exchange preparation procedure and later by protons after reduction of Rh^{3+} to the zero-valent state. The corrosive chemisorption of CO leading to the HF dicarbonyl species might involve the replacement of protons with $Rh^+(CO)_2$ species which act as neutralizing cations for the structure. This fits well with the observed accelerating effect of oxygen and the lack of influence of water on the HF dicarbonyl species. This suggestion also explains why formation of the high-frequency dicarbonyl species is observed for molecular sieve-supported Rh and not for Rh catalysts prepared from impregnation of simple oxide supports.

Several other pieces of information support this suggested structure for the high-frequency dicarbonyl species. In a radial electron distribution study of Rh/Y by Bergeret *et al.* (*10*), it was suggested that oxidized samples contained Rh ions occupying zeolite cation sites in addition to Rh ions bridging extraframework oxygen anions as in conventional oxide clusters. A ^{13}C NMR study (*19*) comparing ion-changed Rh/Y with Rh/SiO_2 noted that the CO–Rh species was bound tightly to the zeolite framework but exhibited only a weak interaction with the SiO_2 support. In another

TABLE 2

OC–Rh–CO Angles for HF[a] and LF Rh Dicarbonyl Species as a Function of Type of Support

Support	Angle (°)	Channel size (nm)[b]	Ref. (for θ)
SAPO-5	110	0.73	This work
Mordenite	79	0.67	This work
NaX	114	0.74	*11*
NaY	112	0.74	*11*
NaY	110	0.74	est. from (*9*)
NaY	110	0.74	est. from (*16*)
NaY	90	0.74	est. from (*10*)[c]
SiO_2	90	—	This work
Al_2O_3	90	—	Est. from (*1*)
Al_2O_3	85	—	Est. from (*6*)
Al_2O_3	75	—	Est. from (*4*)
TiO_2	76	—	*11*

[a] HF angle is given for all molecular sieve supports except Na*X*.

[b] From "Atlas of Zeolite Structure Types" (W. M. Meier and D. H. Olson, Eds.), Butterworths, London, 1987.

[c] Catalyst reduced from Rh^{3+} without hydrogen.

study involving ion-exchanged Rh/Y (*4*), CO adsorption was carried out directly over the unreduced Rh^{3+} neutralizing cations. IR spectra of the Rh–CO species which formed as CO began to reduce the Rh^{3+} species showed exclusively very sharp peaks for the HF dicarbonyl species, further suggesting that this species is closely tied to the cationic sites of the zeolite framework.

While coadsorbed oxygen accelerated the formation of the HF dicarbonyl species at the expense of linear CO, it had no effect on bridge CO. Apparently the larger crystallites on which the bridge CO forms were impervious to the oxidative processes which CO underwent on smaller crystallites. On Rh supported on mordenite, however, a new peak near 2011 cm^{-1} appeared in addition to the HF dicarbonyl, and both species were enhanced in the presence of oxygen. This peak has been assigned previously to bridge CO on oxidized Rh crystallites (*20*), hence demonstrating that it is possible for Rh oxide to remain stable in the form of crystallites or oxide clusters.

The lack of an effect of water on the formation of dicarbonyl species appeared at first glance to be at odds with other reports in the literature. Water vapor added to Rh/Al_2O_3 catalysts which had been dried at extremely elevated temperatures resulted in a distinct enhancement of the low-frequency dicarbonyl species. The low-frequency dicarbonyl species on Rh/SAPO-5 had only weak intensity and was not significantly influenced by any conditions of this work. However, the SAPO-5 support used in this study was exposed to temperatures no greater than 873 K in calcination and reduction steps, a temperature significantly lower than those used (up to 1273 K) in the Rh/Al_2O_3 study mentioned above. SAPO-5 is also hydrophilic, and may return to a hydrated state during exposure to air prior to the 673-K re-reduction. This hydrated state may account for the lack of effect of water on the LF dicarbonyl.

Addition of excess water to Rh zeolite catalysts was noted in some studies to cause the coalescence of isolated Rh into Rh carbonyl molecules such as $Rh_6(CO)_{16}$ within the zeolite pores (*2*). However, it was shown that the $Rh_6(CO)_{16}$ species fully occupied the larger diameter of the supercage Y zeolite. The SAPO-5 pore structure cannot accommodate these large molecules, and hence the HF dicarbonyl remains unaffected by the presence of water.

Both coadsorption of hydrogen and deposition of carbon on the Rh surface appeared to inhibit the formation of the high-frequency dicarbonyl species, in agreement with other work (*21*). These coadsorbates did not affect the frequency of linear CO adsorption contrary to reports that have indicated that both species cause a downward shift in the frequency of linear CO. It has been suggested (*22*) that electron-donating tendencies of these adsorbates to Rh result in increased back-bonding between CO and the metal, causing a downward shift in the observed IR frequency. In the case of hydrogen as a coadsorbate, these studies have demonstrated the existence of a Rh carbonyl hydride, H–Rh–CO.

Neutral adsorption of hydrogen atoms on Rh atoms would not be expected to affect CO frequencies since the electronegativity of H_2 (2.2) is identical to that of Rh. Carbon, however, with an electronegativity of 2.6, could be expected to impart an electron-withdrawing influence on CO adsorbed on Rh as it has been observed to do with other metals of lower electronegativity such as Ni (1.8), resulting in *higher* CO wavenumbers (*23*). No shifts in either direction were observed in the case of Rh/SAPO-5, suggesting that electronic effects of coadsorbates did not play a role in this system. Similarly, the loss of CO dipole–dipole interactions suggested by some workers (*24, 25*) to explain downward shifts for H_2/CO coadsorption were apparently not in effect for Rh/SAPO-5. Lack of CO–CO interaction may imply the presence of small crystallites without high concentrations of sites for linear CO.

Rapid isotopic exchange of dicarbonyl CO on oxidized Rh/SAPO-5 indicated that both high- and low-frequency dicarbonyl species were highly labile, much more so than the bridge CO species. Yet the CO ligands of the high-frequency dicarbonyl species are held tenaciously to the isolated Rh cations even under vacuum at temperatures as high as 573 K, as was seen in Fig. 5. This high-temperature persistence of strongly held dicarbonyl was also seen by Takahashi and coauthors (*19*). As mentioned earlier, their ^{13}C-NMR studies showed that a strong interaction occurred between Rh dicarbonyl species and the framework of the Y-zeolite support at high temperatures (423 K was the highest temperature used in that study) but that a weaker interaction occurred at ambient temperature. They suggested that a reversible process occurred in which the Rh acted as a neutralizing cation for the structure at high temperature and was replaced by a proton at low temperature (*19*):

$$\text{zeo-O-Rh}^+(\text{CO})_2 + \text{H}_2\text{O} \leftrightarrow \text{zeo-O-H} + \text{Rh}^+(\text{OH})(\text{CO})_2.$$

Thus the high temperature adsorption–desorption experiments provide further evidence for the assignment of Rh ions acting as neutralizing cations as the high-frequency dicarbonyl species.

The bond angle for the HF dicarbonyl species on Rh/SAPO-5 resembles that for the same species on Y zeolite, while the Rh/mordenite, with a structure more closely related to the SAPO-5, exhibited a much smaller bond angle. This suggests that geometric factors such as pore size and structure are less important than other parameters in determining the dicarbonyl angle. The similarity in angles for SAPO-5 and the zeolites matches the close agreement in the acidity for these supports, all of which are mildly acidic. This factor appears to be of more importance than the incorporation of phosphorous in the support composition or the structure of the support. The mordenite support of similar structure to SAPO-5 is more strongly acidic and it exhibits a much smaller dicarbonyl angle. Increasing acidity of aluminosilicate supports has been related to increasing electron-deficiency of supported metals (*26, 27*), altering the strength of CO adsorption. Observation of the intensity ratio for dicarbonyl species on molecular sieve-supported Rh catalysts may therefore provide a means of assessing the strength of the acidity and the metal–support interaction.

CONCLUSIONS

The adsorption of CO on SAPO-5-supported Rh was studied in comparison with other supported Rh catalysts. The formation of a high-frequency dicarbonyl species was observed, as has been noted before for molecular sieve-supported Rh. This species was related to the presence of oxygen rather than water as had been previously suggested. It is proposed that this dicarbonyl species acts as a neutralizing cation for the anionic SAPO-5 structure. The OC–Rh–CO angle for the dicarbonyl species on the SAPO-5 support is closer to that for NaY than it is for the highly acidic, but structurally more similar, mordenite support.

Coadsorption of H_2O, H_2, or C with CO on Rh/SAPO-5 had no effect on the frequency of linear or bridge CO adsorption, suggesting that neither electronic nor coverage effects were important factors. These studies not only provided the first characterization of CO species on SAPO-supported Rh, but also helped to bring observations made in other studies of supported Rh into a more coherent picture of the interaction of CO with Rh on molecular sieve and amorphous supports.

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Note added in proof. After this paper was accepted, an experiment was made which further supported the suggestion that the HF dicarbonyl species acts as the neutralizing cation for the SAPO-5 structure. A second ion-exchange procedure was performed on a sample of *reduced* Rh/SAPO-5 in which the protons were exchanged for K^+ cations. Following re-reduction in H_2, this sample was exposed to CO. IR spectra taken over time for this K^+-exchanged sample revealed *no* formation of the HF dicarbonyl species. Suppression of this species could be due to the greater difficulty that $Rh^+(CO)_2$ would have in displacing K^+ vs H^+ as neutralizing cations. Suppression of the HF dicarbonyl in this case supports its assignment as a species acting as a neutralizing cation for molecular sieve supports.

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