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Effect of Coadsorption of CO on the Adsorption of H_2 on Rh/TiO_2

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The effect of CO preadsorption upon the adsorption of H_2 has been studied by magnetic resonance and volumetric methods. CO preadsorption is found to inhibit adsorption of "spillover" hydrogen. Increased hydrogen uptake is interpreted in terms of formation of surface structures associated with the CO.

INTRODUCTION

The study of the species present on a catalytic surface which has been subjected to a variety of treatments is necessary to describe the manner in which catalytic processes occur. Classical spectroscopic studies have been used quite successfully to identify adsorbed species (*1*) as have a large number of ultrahigh-vacuum scattering techniques (*2*). Proton nuclear magnetic resonance spectroscopy (NMR) has been used to study hydrogen-containing species on catalysts and can give valuable information on structure (*3*) of adsorbates, on dynamic states of the proton-containing species (*4*), and on exchange occurring over the catalyst (*5*). We have recently reported the observation by NMR spectroscopy of two types of hydrogenic species on the reduced Fischer–Tropsch catalyst Rh/TiO_2 (*6, 7*). The presence of paramagnetic Ti^{3+} in the support allows one to distinguish between a support-associated species and one associated with the rhodium, via the large upfield shift of the resonance of the support-associated species through its interaction with the paramagnetic centers in the support. This support-associated species is reversibly bound and is believed to arise via "spillover" mechanisms (*8*). We report here the inhibition of the "spillover" adsorption of hydrogen on Rh/TiO_2 by the preadsorption or coadsorption of carbon monoxide. The preadsorption of CO, however, increases the total uptake of H_2 by the catalyst, through creation of a new species.

METHODS

The NMR spectrometer used in this study operates at 56.4 MHz for protons, and has been described previously (*6, 7*). For each spectrum, 500 transients were recorded with Fourier transformation being performed in an on-line PDP-11 minicomputer. ESR spectra were recorded with a Varian E-109 spectrometer operating at a nominal frequency of 9.3 GHz.

The preparation of the catalyst has also been described previously (*6, 7*). The catalyst is 3.8% (by weight) rhodium with a H_{irr}/Rh ratio of 0.6. After preparation, the catalyst was calcined at 400°C for 2 h under flowing O_2. After calcination, the catalyst was reduced at 300°C for 2 h under flowing H_2. Before adsorption of H_2 and CO, the catalyst was outgassed at the reduction temperature to a pressure of 10^{-5} Torr (1 Torr = 133.3 N/m^2). Adsorption was carried out in a glass vacuum system, and the pressure was monitored with a capacitance manometer. Catalyst treatment was carried out in a specially designed reactor, which could be removed from the adsorption apparatus and inserted directly into the NMR and ESR spectrometers. This procedure eliminates transfer problems.

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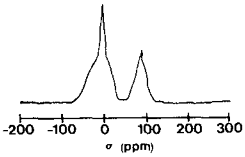

FIG. 1. The ^1H NMR spectrum of H_2 (150 Torr) on Rh/TiO_2 reduced at 300°C. Full spectral width: 500 ppm.

RESULTS

The ^1H NMR spectrum of the catalyst following adsorption of 150 Torr of H_2 is shown in Fig. 1. Two resonances are apparent in the spectrum. The downfield resonance is that of the rhodium-associated species, while the upfield resonance is associated with a species on the support and is assigned to "spillover" hydrogen. Ti^{3+} centers are known to exist under these conditions and are easily detectable with ESR spectroscopy. Figure 2 shows the ESR spectra of the catalyst which has been reduced at 300°C under two conditions: Spectrum A is the spectrum of the catalyst with no adsorbates on the surface, the broad anisotropic signal being due to the resonance of Ti^{3+} at the surface. Spectrum B is that of the same catalyst after the adsorption of 150 Torr of CO. The important point of these results is that the adsorption of CO leaves the Ti^{3+} centers of the support unaltered. No support oxidation to Ti^{4+} has occurred.

Despite the continued presence of paramagnetism in the support after CO adsorption, NMR spectra of the catalyst–adsorbate preparation after the addition of 150 Torr of H_2 do not indicate the presence of a substantial population of the paramagnetically shifted "spillover" hydrogen species (Fig. 3). The resonant absorption is observed in the region where the resonance of protons which are irreversibly bound is seen to occur (Fig. 1). In addition, the intensity of this signal is larger than the resonance of the irreversibly bound hydrogen of Fig. 1 by almost a factor of 2. Taken in conjunction with the ESR results, these NMR results indicate that the preadsorption of CO on the catalyst (1) inhibits the formation of "spillover" hydrogen and (2) produces additional species whose NMR resonances occur in the downfield region. In a separate experiment, we repeated the procedure with the exception that we coadsorbed an equimolar mixture of CO and H_2.

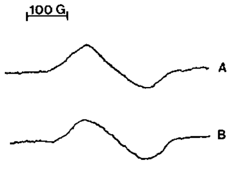

FIG. 2. ESR spectra of Rh/TiO_2 reduced at 300°C. (A) Fresh catalyst with no adsorption. (B) Catalyst with adsorption of CO (150 Torr). Full spectral width: 500 G.

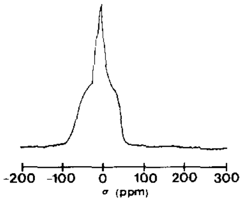

FIG. 3. The ^1H NMR spectrum of H_2 (150 Torr) on Rh/TiO_2 reduced at 300°C with CO having been preadsorbed (100 Torr). Full spectral width: 500 ppm.

Despite the continued presence of paramagnetism in the support, and the opportunity of hydrogenic species formation concurrently with adsorption of the CO, the ^1H NMR spectrum of this catalyst–adsorbate preparation shows the presence of no paramagnetically shifted hydrogenic species.

To determine how the adsorption of CO affects the preadsorbed hydrogen, the following experiment was performed. To the evacuated and reduced catalyst was added H_2 at 150 Torr. This was followed by the adsorption of CO, again at 150 Torr. The NMR spectrum of the resulting material is shown in Fig. 4. The spectrum indicates the presence of the "spillover" hydrogen, even though CO is present in the preparation. The adsorption of CO after H_2 does not seem to inhibit the production of the support associated species, indicating that CO does not merely occupy sites where the "spillover" hydrogen may ultimately interact with the paramagnetic centers, but rather seems to block the pathway by which the "spillover" hydrogen reaches the support.

Volumetric studies were also performed on the catalyst. Figure 5 shows the adsorption isotherms of H_2 on Rh/TiO_2. Curve A is the total uptake of H_2 by a freshly prepared catalyst. After obtaining Curve A, the sample is outgassed at room temperature, which removed any reversibly bound hydrogen. A repeated adsorption measurement at this point produces Curve B, which represents the uptake of reversibly bound hydrogen by the catalyst. We have shown that this uptake corresponds to the production of the support-associated species (*6, 7*). For a second experiment, the catalyst is regenerated by the methods described above. After cooling the catalyst to room temperature, the catalyst is first equilibrated with CO at a pressure of 100 Torr. The sample is then evacuated and the H_2 adsorption isotherms are repeated. The initial adsorption is shown as Curve C in Fig. 5. Total H_2 uptake has nearly doubled, as compared to Curve A. The sample is outgassed at room temperature to remove any reversibly bound hydrogen. Isotherm D in Fig. 5 is the result of measuring the uptake of hydrogen at this point. Very little hydrogen is taken up, indicating that the CO adsorption has effectively quenched the production of the reversibly bound hydrogen.

One may speculate on the mechanism whereby CO inhibits the formation of "spillover" hydrogen. It has been shown that the adsorption of CO on Rh is much stronger than that of hydrogen (*11*). In addition, Yates *et al.* (*12*) have shown that the room temperature adsorption of CO on isolated Rh atoms on an Al_2O_3 support is of a bidentate type with two CO's adsorbed per metal atom. It has also been suggested that edge atoms on Rh rafts may also be able to adsorb two CO's per metal atom (*13*). It seems reasonable to assume that the production of "spillover" hydrogen occurs at these isolated atoms and raft edges, since it is these atoms which are closest to the support. If such is the case, the presence of the dicarbonyl structure may sterically impede the dissociative adsorption of hydrogen at these points, resulting in very little "spillover" hydrogen being produced. The NMR results on the preadsorption of CO are consistent with this picture. In addition, the results also indicate that the dissociative adsorption cannot occur even when H_2 and CO are simultaneously coadsorbed in a 1:1 molar ratio. The fact that "spillover" hydrogen is produced when H_2 is adsorbed, followed by CO adsorption, indicates that CO must block the pathway but does not significantly interfere with the "spillover" hydrogen once it is on the surface. This is also consistent with this picture of the mechanism of dissociative adsorption. It may be that, given enough time, CO will begin to replace hydrogen on the surface of the metal due to its higher affinity for metal

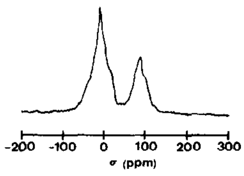

FIG. 4. The ^1H NMR spectrum of H_2 (150 Torr) on Rh/TiO_2 reduced at 300°C. CO (100 Torr) was adsorbed after H_2. Full spectral width: 500 ppm.

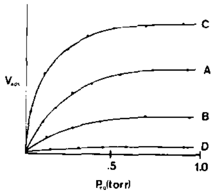

FIG. 5. Adsorption isotherms for H_2 on Rh/TiO_2. (A) Total uptake of H_2 by a fresh catalyst. (B) H_2 uptake after outgassing at room temperature. (C) Total uptake of H_2 for a catalyst prepared by CO preadsorption. (D) Uptake of H_2 after outgassing of the catalyst of (C) at room temperature.

binding (*14*), but we see no indication of this process occurring on the time scale of a few days.

A number of structures have been proposed to occur when CO and H_2 are coadsorbed at room temperature, such as surface enols (*15*) and surface hydrocarbons (*16*) produced via a surface carbide intermediate. The presence of any of these species on the surface can account for the increased uptake of hydrogen when CO is first adsorbed on the catalyst, as well as for the additional intensity observed in the ^1H spectrum in the region where hydrocarbon resonances occur. Closer examination of Fig. 3 shows that there are at least two resonances in the spectrum, a comparatively "sharp" one superimposed on a somewhat broader one. By comparison with the spectrum for the material having only hydrogen on the surface (Fig. 1), one sees that the "sharp" resonance seems to be the resonance of the species adsorbed in the original experiments. Thus, the remaining intensity must result from the formation of the species requiring the presence of CO and which accounts for the additional uptake in the volumetric adsorption experiments. With the resolution obtainable, it is not possible to distinguish the nature of the intermediate, but is is not associated with the paramagnetic centers in the surface.

CONCLUSIONS

The coadsorption of H_2 and CO produces a catalyst–adsorbate system whose ^1H NMR spectrum is markedly different from that of a catalyst with only hydrogen adsorbed (*6, 7*). The preadsorption of CO inhibits the formation of the support-associated species found earlier, but increases the total adsorption of H_2 by forming a new species observable by NMR spectroscopy, which could be any of a number of proposed species. The NMR results are consistent with infrared and ^{13}C NMR studies of a similar catalyst system (*12, 13*). The present NMR results are consistent with the picture of "spillover" hydrogen production being inhibited by the presence of bidentate carbonyl species at points where dissociative adsorption of hydrogen produces this "spillover" species.

ACKNOWLEDGMENTS

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REFERENCES

1. Delgass, W., Haller, G., Kellerman, R., and Lunsford, J., "Spectroscopy in Heterogeneous Catalysis." Academic Press, New York, 1979.

2. For example, see Somorjai, G., and van Hove, M., "Adsorbed Monolayers on Solid Surfaces." Springer-Verlag, Berlin, 1979.

3. Lechert, H., and Wittern, K., *Ber. Bunsenges. Phys. Chem.* **84,** 596 (1979).

4. Pfeifer, H., *in* "NMR: Basic Principles and Progress" (P. Diehl *et al.*, Eds.), Vol. 7, p. 1. Springer-Verlag, Berlin/New York, 1972.

5. Cirillo, A., Dereppe, J., and Hall, W., *J. Catal.* **61,** 170 (1980).

6. Gajardo, P., Apple, T., and Dybowski, C., *Chem. Phys. Lett.* **74,** 306 (1980).

7. Apple, T., Gajardo, P., and Dybowski, C., *J. Catal.* **68,** 103 (1981).

8. (a) Wilson, G., and Hall, W., *J. Catal.*, **17,** 190 (1970); (b) Fleisch, T., and Abermann, P., *J. Catal.* **50,** 268 (1977).

9. Kramer, R., Andre, M., *J. Catal.* **58,** 287 (1979).

10. Vaughan, R., Elleman, D., Stacey, L., Rhim, W., and Lee, J., *Rev. Sci. Instrum.* **43,** 1358 (1972).

11. Hayward, D., *in* "Chemisorption and Reactions on Metallic Films" (J. Anderson, Ed.), Vol. 1, p. 225. Academic Press, New York, 1971.

12. Yates, J., Duncan, T. M., and Vaughan, R., *J. Chem. Phys.* **71,** 3908 (1979).

13. Yates, D. J. C., Murrell, L. L., Prestridge, E. B., *J. Catal.* **57,** 41 (1979).

14. McKee, D., *J. Catal.* **8,** 240 (1967).

15. Vannice, M., *J. Catal.* **37,** 462 (1975).

16. Ekerdt, J., Bell, A., *J. Catal.* **58,** 170 (1979).