

## Infrared Spectroscopic Evidence for CO Dissociation on NaX-Zeolite-Supported Rhodium

The dissociation of CO in rhodium is a matter of intense discussion because of its significance for the activity and selectivity of CO hydrogenation on Rh catalysts. Rhodium is situated at the borderline between metals on the left side of the Periodic Table on which the adsorption of CO is dissociative and those on the right side on which the adsorption of CO is molecular (1). There are some contradictions in the results obtained for the adsorption and dissociation of CO on single crystal planes and polycrystalline material of Rh. Somorjai and co-workers found CO dissociation by heating a Rh foil in a low-pressure atmosphere of CO (2-4). Especially effective for the dissociation were planes like Rh(331) and Rh(755) which exhibit a great number of steps and kinks. On the other hand, Yates and co-workers (5, 6) and Gorodetskii and Nieuwenhuys (7) concluded from their results that there was only a very small probability for CO dissociation on rhodium crystal planes.

Concerning supported rhodium, it seems to be confirmed that CO dissociates at least at higher temperatures on reduced forms. Solymosi and Erdöhelyi (8) have found by a microcatalytic pulse technique that on Rh/Al<sub>2</sub>O<sub>3</sub> there is CO dissociation at temperatures higher than 473 K. In a recent paper (9) they extended their investigation to Rh on other supports, viz., TiO<sub>2</sub>, SiO<sub>2</sub>, and MgO, and found the formation of CO<sub>2</sub> from the disproportionation (dissociation) of CO on Rh above 473 K to be in the order TiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub> > MgO for the supports. Similar results were obtained by Niwa and Lunsford (10) at temperatures higher than 573 K and they included Y-zeolite as a sup-

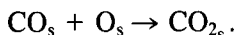
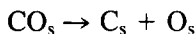
port. From the appearance of carbonate bands in the IR spectra Iizuka *et al.* concluded that dissociation of CO occurred on Rh/Al<sub>2</sub>O<sub>3</sub> at temperatures higher than 373 K whereas on Rh/ZrO<sub>2</sub> the dissociation seemed to appear at lower temperatures (~313 K) to a very small extent. On Rh/MgO they could not find any carbonate bands due to CO dissociation (11, 12).

In the present work we investigated the dissociation of CO on Rh supported on NaX-zeolite. The reason for the choice of NaX was first the importance of NaX as a support in several catalytic reactions involving CO as reactant. Second, CO<sub>2</sub> formed during the CO disproportionation (dissociation) is easily adsorbed by the X-zeolite and can be detected unambiguously by IR spectroscopy in the form of well-known carbonate structures (13).

The catalyst was prepared by ion exchange of NaX-zeolite (13 X Wolfen) with an aqueous solution of [Rh(NH<sub>3</sub>)<sub>5</sub>Cl](OH)<sub>2</sub> and subsequent drying and calcining in air (2 h, 673 K). The metal content was 1 wt% Rh. According to H<sub>2</sub> chemisorption the dispersion of the reduced catalyst was about 1 (ratio H:Rh). For IR spectroscopic measurements the catalyst was pressed to self-supported wafers (10-15 mg/cm<sup>2</sup>) and placed in a conventional cell. All pretreatments were performed *in situ* and particular care was taken to prevent any admission of air or moisture. As CO<sub>2</sub> is formed in the reaction of supported Rh(III) species with CO (14), the catalysts were reduced carefully at 673 K with hydrogen. During the reduction water was removed with a liquid-nitrogen trap. The gases used were of high purity (CO: 99.997%, Ferak, H<sub>2</sub>:99.999%,

Tega). The IR spectra were recorded by an UR-20 double-beam spectrometer (Zeiss, Jena, DDR).

In a first series of experiments CO was admitted alone to the catalyst. The results are shown in Figs. 1a–g. At beam temperature (ca. 313 K) the spectrum shows only distinct bands due to adsorbed CO on supported rhodium: there are strong bands at 2100 and 2000  $\text{cm}^{-1}$  due to the twin structure  $\text{Rh}(\text{CO})_2$ , and in addition a shoulder at 1950  $\text{cm}^{-1}$  and a broad band at about 1800  $\text{cm}^{-1}$ , both probably due to bridge-bonded CO. Only after raising the temperature to 373 K were distinct bands obtained at 1430 and 1488  $\text{cm}^{-1}$  (Fig. 1d) which could be assigned to a carbonate structure on the NaX support (13). Apparently, in these conditions the CO molecules dissociate on the Rh/NaX sample and  $\text{CO}_2$  is formed and adsorbed as carbonate on the NaX support:



An interaction of CO with the pure NaX support at the same conditions does not

yield a significant amount of surface carbonate. Even after a treatment with CO at 423 K for 30 min the carbonate bands have a very low intensity comparable with Fig. 1b.

Interestingly, after short evacuation of the CO-covered Rh/NaX at 373 K the intensity of the carbonate band increases significantly (Fig. 1e). The absorbance of the 1488- $\text{cm}^{-1}$  band increases from 0.07 to 0.12. The reason for this increasing intensity may be the stronger interaction of the remaining CO groups with the Rh atoms. This would result in a weakening of the CO bond and, therefore, in a higher dissociation probability. This explanation is supported by the shift of the absorption bands of the bridge-bonded CO groups to lower wavenumbers by 5–10  $\text{cm}^{-1}$  (Fig. 1e). This frequency shift during evacuation may also be interpreted in terms of decreased dipole–dipole interactions (15) but an electronic effect seems to operate simultaneously (16). The increasing dissociation probability at lower CO coverage results in the formation of carbonate bands also at beam temperature (ca. 313 K) to a very small extent (Fig. 1c).

At higher temperatures  $\text{CO}_2$  is desorbed (17) and the intensity of the carbonate bands decreases, especially at temperatures higher than 423 K (Figs. 1f, g). This desorbed  $\text{CO}_2$  could be found by a separate temperature-programmed desorption experiment with detection by a mass spectrometer. CO was adsorbed at room temperature on a sample that had previously been reduced and outgassed at 673 K. On raising the temperature CO desorbs and, beginning at about 473 K together with CO also  $\text{CO}_2$  is detected in the gas phase with increasing concentration up to 823 K.

In a second series of experiments CO was admitted together with  $\text{H}_2$  to the catalyst (Fig. 1h). Evidently, the dissociation of CO is promoted to hydrogen and the carbonate structures appear distinctly at 313 K. The promotion of the CO dissociation on supported Rh catalysts by adsorbed hydrogen was already mentioned by Solymosi

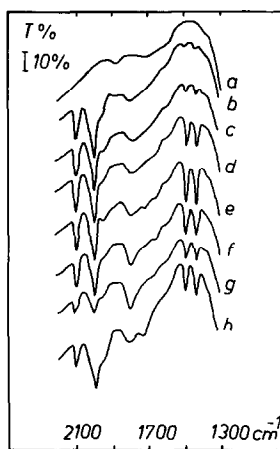


FIG. 1. Infrared spectra of the interaction of CO with Rh/NaX (1 Torr = 133.3  $\text{N m}^{-2}$ ). (a) Background: reduced at 673 K with  $\text{H}_2$ , evacuated at 673 K; (b) 8 Torr CO at 313 K for 50 min, after (a); (c) after evacuation at 313 K; (d) 373 K for 10 min after (c); (e) after evacuation at 373 K; (f) 423 K for 10 min after (e); (g) 473 K for 10 min after (f); (h) 9 Torr CO + 16 Torr  $\text{H}_2$  at 313 K for 25 min after (a).

*et al.* (18). We agree with their assumption that the electron-donating properties of adsorbed hydrogen may result in a weakening of the CO bond due to the higher  $\pi$ -back-bonding and may therefore be the reason for the CO dissociation at lower temperatures.

On the other hand, hydrogen may promote the CO dissociation by removing the reaction products from the active sites. As oxygen is removed by CO, hydrogen could remove the active carbide species.

The role of hydrogen is also discussed in terms of hydrogen-assisted dissociation via hydrogen-containing intermediates such as formyl or hydroxycarbene species (19–21). However, in that case we should expect water as the main oxygen-containing product. The spectrum (Fig. 1h) does not support this possibility. It seems that the final conclusion on the influence of hydrogen needs further investigations.

To summarize, it has been shown that CO dissociates on Rh/NaX to a significant amount at a temperature of 373 K and higher. Hydrogen promotes this reaction and causes a dissociation already at 313 K. The dissociation is also favored by a decreased CO coverage on the surface of the catalysts.

## REFERENCES

1. Brodén, G., Rhodin, T. N., Brucker, C., Benbow, R., and Hurych, Z., *Surf. Sci.* **59**, 593 (1976).
2. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46**, 167 (1977).
3. Castner, D. G., and Somorjai, G. A., *Surf. Sci.* **83**, 60 (1979).
4. Castner, D. G., Dubois, L. H., Sexton, B. A., and Somorjai, G. A., *Surf. Sci.* **103**, L 134 (1981).
5. Yates, J. T., Williams, E. D., and Weinberg, W. H., *Surf. Sci.* **91**, 562 (1981).
6. Yates, J. T., Williams, E. D., and Weinberg, W. H., *Surf. Sci.* **115**, L 93 (1982).
7. Gorodetskii, V. V., and Nieuwenhuys, B. E., *Surf. Sci.* **105**, 299 (1981).
8. Solymosi, F., and Erdöhelyi, A., *Surf. Sci.* **110**, L 630 (1981).
9. Erdöhelyi, A., and Solymosi, F., *J. Catal.* **84**, 446 (1983).
10. Niwa, M., and Lunsford, J. H., *J. Catal.* **75**, 302 (1982).
11. Iizuka, T., Tanaka, Y., and Tanabe, K., *J. Mol. Catal.* **17**, 381 (1982).
12. Tanaka, Y., Iizuka, T., and Tanabe, K., *J. Chem. Soc. Faraday Trans. 1* **78**, 2215 (1982).
13. Bertsch, L., and Habgood, H. W., *J. Phys. Chem.* **67**, 1621 (1963).
14. Primet, M., Védrine, J. C., and Nacchache, C., *J. Mol. Catal.* **4**, 411 (1978).
15. Primet, M., *J. Catal.* **88**, 273 (1984).
16. Heskett, D., Plummer, E. W., and Messmer, R. P., *Surf. Sci.* **139**, 558 (1984).
17. Nabiev, B. A., Lafer, L. I., Jakerson, V. I., and Rubinstejn, A. M., *Izv. Akad. Nauk SSSR, Ser. Chim.* 1461 (1976).
18. Solymosi, F., Tombacz, I., and Kocsis, M., *J. Catal.* **75**, 78 (1982).
19. Wang, S.-Y., Moon, S. H., and Vannice, M. A., *J. Catal.* **71**, 167 (1981).
20. Mori, T., Masuda, H., Imai, H., Miamoto, A., Hasebe, R., and Murakami, Y., *J. Phys. Chem.* **87**, 3648 (1983).
21. Bianchi, D., and Bennett, C. O., *J. Catal.* **86**, 433 (1984).

D. GUTSCHICK  
H. MIESSNER

Central Institute of Physical Chemistry  
Academy of Sciences of the  
German Democratic Republic  
Rudower Chaussee 5  
DDR-1199 Berlin, Germany (DDR)

M. WEBER

VEB Leuna-Werke "Walter Ulbricht"  
DDR-4200 Leuna  
Germany (DDR)

Received July 16, 1984