

## Reply to Comments on the "Surface Interaction between H<sub>2</sub> and CO<sub>2</sub> on Rh/Al<sub>2</sub>O<sub>3</sub>"

As we mentioned in our earlier paper (1), there is a controversy in the literature concerning the adsorption and dissociation of CO<sub>2</sub> on rhodium surfaces. In contrast to the previous studies, Somorjai *et al.* (2-4) found that CO<sub>2</sub> does chemisorb and dissociate on several faces of a Rh single crystal, but it requires an exposure much higher than that in the case of CO. The dissociation of CO<sub>2</sub> was clearly indicated by the appearance of absorption bands at 2060 (!) and 1870 cm<sup>-1</sup> in the high-resolution ELS spectra of chemisorbed CO<sub>2</sub> on Rh(111) at 300 K (4). The dissociation of CO<sub>2</sub> on Rh/Al<sub>2</sub>O<sub>3</sub> was first discovered by Primet (5). Weak absorption bands appeared at 2025 and 1860 cm<sup>-1</sup>; the lower frequency of terminal CO was attributed to the weak CO coverage!

With regards to our observations on supported Rh, among others we wrote (1): "From our more detailed investigations concerning this question, we found that the dissociation of CO<sub>2</sub> occurs to a small extent on supported Rh, too. The preparation of the catalyst, the dispersity of the Rh, and the nature of the support all have an influence on this process. On the sample used in the present work, weak bands due to CO, indicating the occurrence of dissociation of CO<sub>2</sub>, appeared at 373 K when a high pressure (200 Torr) of CO<sub>2</sub> was used."

Thus, we also observed the dissociation of CO<sub>2</sub> on supported Rh. In this respect we consider the results of Iizuka and Tanaka (6) as confirmation of previous findings on Rh/Al<sub>2</sub>O<sub>3</sub> (1, 5).

On the basis of the results of Primet and our own observations, the most obvious and simplest explanation of the infrared

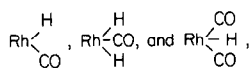
spectra found during the H<sub>2</sub> + CO<sub>2</sub> interaction is that which involves the coverage effect suggested first by Primet (5).

There were, however, a number of observations which led us to believe that the different ir spectrum of adsorbed CO formed in the H<sub>2</sub> + CO<sub>2</sub> interaction cannot be attributed merely to the low coverage of CO. The phenomena of the absence of twin CO and the appearance of terminal CO at lower frequencies on Rh are not unique for the H<sub>2</sub> + CO<sub>2</sub> interaction (or for CO<sub>2</sub> adsorption as Iizuka and Tanaka conclude (6)); the same behavior was experienced in other cases, when adsorbed CO was produced in a surface reaction on Rh.

The decomposition of adsorbed formic acid on alumina-supported Rh (1), and on magnesia-, titania-, and silica-supported Rh (7), yielding CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O as products, gave a CO band at 2030-2040 cm<sup>-1</sup> (!) and a weaker one at 1875 cm<sup>-1</sup>, but never a twin CO band at all. Similar to the case of the H<sub>2</sub> + CO<sub>2</sub> interaction, the band intensity of linear CO was significantly higher than that observed at high CO<sub>2</sub> exposure, but the band still appeared at lower frequency. As the development of formate ion was detected in the H<sub>2</sub> + CO<sub>2</sub> surface interaction, it was further proposed that the formation of CO in the H<sub>2</sub> + CO<sub>2</sub> interaction might occur through the formation and decomposition of surface formate ion (1, 7).

Yates *et al.* (8) found that the dissociative adsorption of formaldehyde on Rh/Al<sub>2</sub>O<sub>3</sub> produced a spectrum which was distinctly different from the spectrum of CO on Rh, where a strong doublet feature at 2101 and 2031 cm<sup>-1</sup> was dominant at com-

parable levels of CO exposure. They observed only a band close to  $1860\text{ cm}^{-1}$  and another one near  $2038\text{ cm}^{-1}$ . As the HCHO exposure was increased, there was an indication of three overlapping features, at 2026, 2048, and  $2066\text{ cm}^{-1}$ . The observed phenomenon was attributed to the formation of the Rh-carbonyl-hydride species,



and to an increased  $\pi$  donation from the Rh into the antibonding  $2\pi$ -CO orbital.

In addition, Yang and Garland (9) found that the presence of hydrogen shifts the  $2062\text{-cm}^{-1}$  band (terminal CO) to lower frequencies,  $2038\text{--}2027\text{ cm}^{-1}$ , at 433 K, without causing any decrease in its intensity (see Figs. 8 and 9 in Ref. (9)).

It is important that when the surface treated with  $\text{H}_2 + \text{CO}_2$  (1, 7), HCOOH (1, 7), or HCHO (8) was exposed to very small doses of CO, the twin CO band appeared at once in all cases.

We believe that the Rh-carbonyl-hydride species are formed both in the surface interaction of  $\text{H}_2 + \text{CO}_2$  and in the decom-

position of surface formate ion, and they contribute greatly to the observed characteristics of the ir spectra of CO formed in all three surface reactions.

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