

LETTERS TO THE EDITORS

Dissociative Adsorption of CO₂ on Supported Rhodium Catalyst:
Comment on Surface Interaction between H₂ and CO₂ on Rh-Al₂O₃

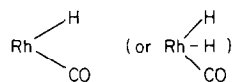
Recently Solymosi *et al.* reported the interaction of CO₂ and H₂ over Rh-Al₂O₃ (1). In the infrared experiments, they observed the formation of adsorbed CO from CO₂ in the presence of H₂, but failed in detecting the band without H₂ under the same condition. Concerning the main difference between the spectrum of adsorbed CO and that obtained after coadsorption of the H₂ + CO₂ mixture, they concluded that (i) the doublet due to twin CO was completely missing, (ii) the linearly bonded CO appeared at lower frequency, ~2020-2039 cm⁻¹.

The present authors also observed the infrared spectra of CO₂ adsorbed on Rh-Al₂O₃, but the result was rather different from that of Solymosi *et al.* As shown in Fig. 1A, carbon dioxide adsorbed on 2.3 wt% Rh-Al₂O₃ which had been reduced at 300°C gave the linear CO species at about 2020 cm⁻¹. The band intensity increased with the adsorption temperature, but the twin and bridged species were not observed even at higher temperature (>200°C). Solymosi *et al.* (1) and the other previous workers (2-4) could not detect the CO band, indicative of the dissociation of CO₂ on Rh metal. However, Somorjai and co-workers found the dissociation of CO₂ on several faces of Rh single crystals in an ultrahigh vacuum system (5, 6). For the reason of the difficulty of detection, Somorjai suggested the low sticking probability of CO₂ and the high rate of the association reaction, CO_{ads} + O_{ads} → CO_{2(g)} (6). In the present work over Rh-Al₂O₃, the dissociation was observed even at room temperature and at a moderate pressure of CO₂ (~2-15 Torr). The CO band was also ob-

served on Rh-ZrO₂ and Rh-MgO, but was not detected on Rh-SiO₂. Probably, the dissociation depends on the nature of the support used, the preparation of the catalyst, and the dispersity of the Rh.

Upon the adsorption of the mixture of CO₂ and H₂, the strong enhancement of the CO band was observed as shown in Fig. 1B, but the band frequency was almost the same as that in the case of pure CO₂ adsorption. Solymosi *et al.* stated,

The absence of the twin structure cannot be attributed to the low surface concentration of CO. It is more probable that the adsorbed hydrogen prevents the formation of the twin structure, and that instead



is formed. The fact that the vibration of this species is somewhat lower than that of unperturbed linearly bonded CO is in agreement with the expectation that the H chemisorbed to the rhodium atom of a carbonyl is electron donating, which increases the π -donation from the rhodium into the antibonding π orbital of the CO, resulting in a decrease in ν_{CO} .

However, in our experiment, the twin species was also completely missing and the band frequency was still lower than that of CO adsorption in the absence of hydrogen. These phenomena are rather characteristic for CO₂ adsorption on Rh metal. Thus the model and explanations for the above-mentioned facts proposed by Solymosi are beside the point. Since it is well known that the band frequency of CO stretching is a strong function of CO coverage (2, 6), the authors are inclined to think that those facts

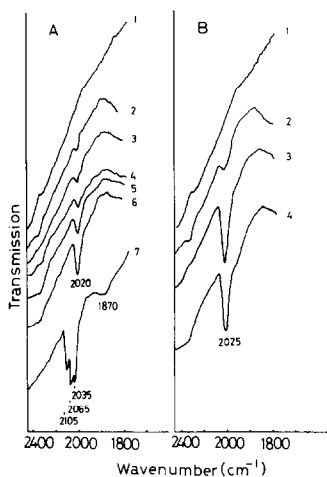


FIG. 1. Infrared spectra observed at room temperature. (A) CO_2 adsorption (5 Torr) on $\text{Rh-Al}_2\text{O}_3$ at different temperatures: (1) background; (2) room temperature; (3) 100°C ; (4) 150°C ; (5) 200°C ; (6) 250°C ; (7) CO adsorption (5 Torr) at room temperature. (B) CO_2 (5 Torr) + H_2 (10 Torr) adsorption at different temperatures: (1) background; (2) room temperature; (3) 100°C ; (4) 150°C .

are due to a small coverage of CO formed from CO_2 on the surface of Rh . The small coverage of CO on the catalyst would be a main cause of the differences in reactivity

and selectivity between $\text{CO} + \text{H}_2$ and $\text{CO}_2 + \text{H}_2$ reactions (7). The detailed study is in progress.

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