

Rate-determining Step in the Methanation of Carbon Monoxide with a Palladium on Alumina Catalyst

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By using i.r. and pulse-dynamic measurements, it has been proved that the rate-determining step in the methanation of CO on a Pd/Al₂O₃ catalyst is the dissociation of the C–O bond of the adsorbed CO species while the hydrogenation of surface carbon species proceeds rapidly.

Attention has been paid recently to the mechanism of hydrogenation of CO from the viewpoint of utilization of coal. Recent investigations have shown that the Fischer–Tropsch synthesis is initiated by the dissociation of the C–O bond of adsorbed CO species to form surface carbon species, *i.e.* adsorbed CH_x ($x = 0, 1, 2, \text{ or } 3$), which is followed by the hydrogenation of the carbon species to form hydrocarbons with various numbers of carbon atoms.¹ However, the nature of the rate-determining step in the Fischer–Tropsch synthesis has not been well established.² Rabo *et al.* have shown that Pd is less active for the dissociation of the C–O bond of the adsorbed CO species than Ni, Co, or Ru,³ suggesting that the rate-determining step in Fischer–Tropsch synthesis on Pd is the dissociation of the C–O bond of the adsorbed CO species. The purpose of this study is to confirm this mechanism by using i.r. dynamic measurements coupled with pulse surface reaction rate analysis (P.S.R.A.).⁴

The dispersion of Pd in the Pd/Al₂O₃ catalyst used (Pd loading, 0.5 wt %; Nippon Engelhardt Ltd) was determined by a conventional CO adsorption method to be 27.5%. *In situ* i.r. measurements were made on a JASCO EDR-31 emissionless diffuse-reflectance i.r. spectrometer (E.D.R.)⁵ under the following conditions: flow rate of H₂, 100 cm³ min⁻¹; flow rate of CO, 0–10 cm³ min⁻¹; reaction temperature, 403–407 K; total pressure, 101.3 kPa; catalyst weight, *ca.* 0.1 g. P.S.R.A. experiments were carried out with the apparatus and procedure described previously⁴ under the following conditions: flow rate of carrier gas (H₂), 40 cm³ min⁻¹; amount of CO pulsed, 0.1–0.4 μmol; reaction temperature, 423–553 K; total pressure, 101.3 kPa; catalyst weight, 0.1 g. Under the present experimental conditions, CH₄ and H₂O were selectively produced by the reaction.

The i.r. spectra of the Pd/Al₂O₃ catalyst under steady-state conditions in the CO–H₂ reaction exhibited bands due to linear CO (2080 cm⁻¹), bridge CO (1900 and 1970 cm⁻¹), formate ion (1380 and 1590 cm⁻¹), and gaseous CO (2120 and 2180 cm⁻¹). No absorption bands were observed in the C–H stretching region. Figure 1(a) shows the relative reflectances of these bands for the reaction at 443 K. Under the steady-state CO–H₂ reaction conditions, the reflectance for each peak did not change with time, indicating constant concentrations of adsorbed species on the catalyst. When the supply of gaseous CO was stopped, the bands due to gaseous CO immediately disappeared while the reflectances for linear CO and bridge CO increased gradually with increasing time. The reflectance for the formate ion remained unchanged. Since the desorption of the adsorbed CO was negligible under the present experimental conditions, these results indicate that the adsorbed CO species are reactive in flowing H₂ and are gradually converted into CH₄ *via* surface carbon species, while the formate ion is inactive. According to the Kubelka–Munk equation,^{5,6} the first-order rate constant for the reaction of each adsorbed species (k) can be determined from the relative reflectance (r) by the equation $k = \text{dln}[r/(1-r)^2]/\text{d}t$. In other words, the slope of the straight line of a plot of $\text{ln}[r/(1-r)^2]$ against time gives the first-order rate constant. The observed values of r shown in Figure 1(a) satisfied this relationship as shown in Figure 1(b). From the slope of the straight line, the rate constant was determined for each species as follows: 1.1 (linear CO), 0.80 (bridge CO at 1900 cm⁻¹), and 2.2 ks⁻¹ (bridge CO at 1970 cm⁻¹).

The rate constant for CH₄ formation per adsorbed CO species was determined by P.S.R.A. as follows.⁴ When a small amount of CO was injected at the inlet of the catalyst bed into

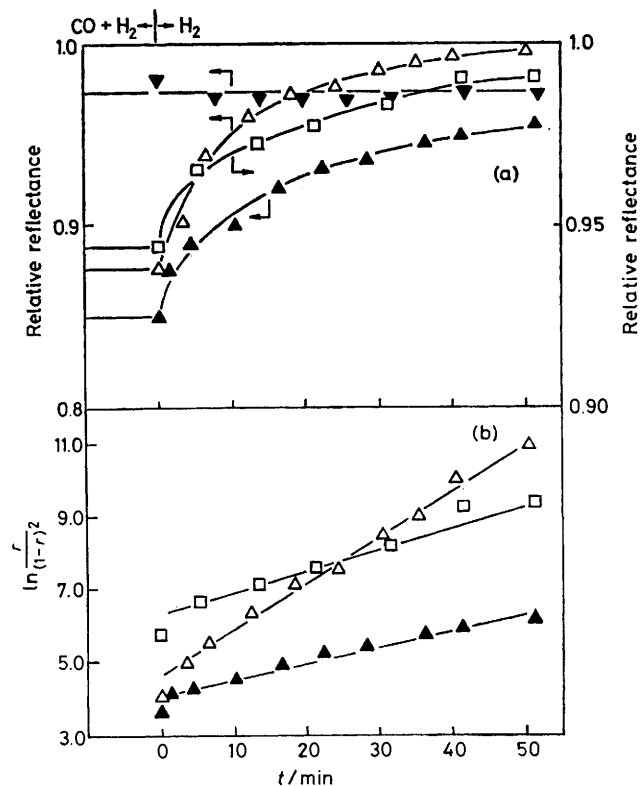


Figure 1. (a) Changes in relative reflectances (r) of various absorption bands for the reaction on a Pd/Al₂O₃ catalyst at 443 K. (b) Relationships between $\ln[r/(1-r)^2]$ and time (t). At $t < 0$, steady state CO-H₂ reaction; flow rates of H₂ and CO 100 and 10 cm³ min⁻¹, respectively. At $t = 0$, the CO gas supply was stopped and the H₂ flow rate remained 100 cm³ min⁻¹. At $t > 0$, hydrogenation of the adsorbed CO took place. \blacktriangle , bridge CO at 1900 cm⁻¹; \triangle , linear CO at 2060 cm⁻¹; and \blacktriangledown , surface formate at 1590 cm⁻¹.

flowing H₂, it was immediately adsorbed on the catalyst and was gradually hydrogenated to form CH₄ and H₂O. The rate of CH₄ formation was continuously measured by a flame ionization detector located at the outlet of the reactor. According to P.S.R.A. theory,^{4,7} the slope of the decay curve

represents the rate constant. The observed rate constant for CH₄ formation thus determined was 1.5 ks⁻¹ at 443 K, which is close to the values determined by E.D.R. experiments. Although Figure 1 shows only data for the reaction at 443 K, similar results were also obtained at other temperatures and the rate constants determined by the E.D.R. method were similar to those determined by P.S.R.A.

These data indicate that the rate of C-O bond dissociation as measured by E.D.R. is almost equal to the rate of CH₄ formation as measured by P.S.R.A. This in turn leads to the conclusion that the rate-determining step is C-O bond dissociation of the adsorbed CO species and that the hydrogenation of the surface carbon species proceeds rapidly. If the C-O bond dissociation proceeded rapidly and the hydrogenation of the surface carbon species were the rate-determining step, the rate constant for C-O bond dissociation measured by E.D.R. should be much larger than that of CH₄ formation measured by P.S.R.A., in conflict with our results. The absence of a C-H stretching band in the i.r. spectra supports the conclusion that the CH_x species are rapidly hydrogenated to CH₄.

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