

LETTER TO THE EDITORS

High Methanation Activity of Titania-Supported Pd Catalyst in the SMSI State

Concerning the hydrogenation of CO on titania-supported metal catalysts, there seems to be serious controversy about the high activity in their strong metal-support interaction (SMSI) state (1). This controversy may have been caused by the evaluation of the activity on the basis of turnover frequency (TOF), which is determined by dividing a reaction rate by the number of active sites. Because of the drastic decrease in the chemisorption ability of the SMSI catalyst (2), it is difficult to determine exactly the amount of H₂ or CO adsorbed and therefore to evaluate the exact number of the active sites on this catalyst (3). In order to confirm the high activity of the SMSI catalyst for CO hydrogenation, one should determine its intrinsic activity on the basis of a quantity other than the conventional TOF.

In their recent study of the interactions of H₂ and CO with Pd/TiO₂ and TiO₂-promoted Pd/SiO₂, Rieck and Bell appeared to find a clue to the solution by using TPSR (temperature-programmed surface reaction), which satisfies the condition mentioned above (4). Because the temperature at which the peak of the TPSR curve occurs can be recognized as a measure of the activity unaffected by the number of active sites, this technique seems to give information about the intrinsic activity of the catalyst system which involves uncertainty over the number of active sites. Their TPSR measurements clearly showed that decoration of Pd by TiO_x moieties, which is accepted as a model of the SMSI catalyst (3, 5), led to the high methanation activity; the peak temperature of the TPSR curve decreased with increasing TiO_x moieties on

Pd/SiO₂. In spite of their excellent idea, however, it seems that their study does not lead directly to the solution of the high activity of the SMSI catalyst, because for Pd/TiO₂ the peak temperature increased with increasing reduction temperature, indicating the suppression of methanation.

We have developed the pulse surface reaction rate analysis (PSRA) method in order to determine the reaction rate per active site and demonstrated its applicability to CO hydrogenation (6). This technique also meets the requirement mentioned above, because the rate constant for CO hydrogenation can be determined directly without any information about the number of active sites on the catalyst. By applying this method to methanation on titania-supported noble-metal catalysts, we find unambiguously that the intrinsic activity of the Pd and Pt catalysts in their SMSI state is 5 to 10 times larger than that in their normal state, although, on these catalysts, as a consequence of SMSI, the chemisorption ability for CO decreases to ca. $\frac{1}{10}$ of the original amount (7).

The discrepancy between our results and those of Rieck and Bell may be ascribable to the difference in the reduction temperature. The highest reduction temperature used by Rieck and Bell was only 673 K, which seems to be slightly low to bring a catalyst to the SMSI state completely. Our catalyst, on the other hand, was reduced at 773 K, thereby bringing it to the SMSI state, as confirmed by CO adsorption (7). In Fig. 1, the amount of CO adsorbed and the rate constant for methanation determined by PSRA are plotted against the reduction temperature of titania-supported

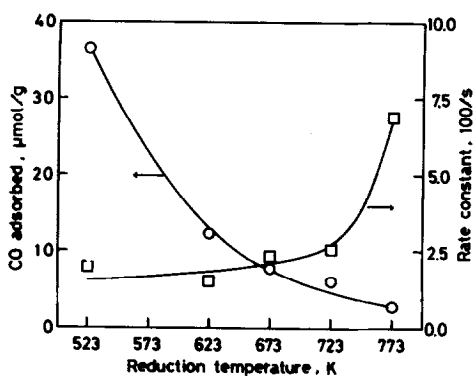


FIG. 1. Effect of reduction temperature on the amount of CO adsorbed (○) and the rate constant for methanation determined by PSRA at 498 K on 1.0 wt% Pd/TiO₂ (□). Prior to measurement, the catalyst was heated in flowing O₂ at 723 K for 2 h, followed by reduction at various temperatures for 2 h.

Pd catalyst (8). As shown, although reduction at 673 K results in a significant decrease in adsorption ability, this temperature is not necessarily high enough to lead to activity enhancement. The intrinsic methanation activity is remarkably enhanced just after reduction above 773 K.

REFERENCES

- Vannice, M. A., and Garten, R. L., *J. Catal.* **56**, 236 (1978); Wang, S-Y., Moon, S. H., and Vannice, M. A., *J. Catal.* **71**, 167 (1981); Burch, R., and Flambard, A. R., *J. Catal.* **78**, 389 (1982); Vannice, M. A., and Twu, C. C., *J. Catal.* **82**, 213 (1983); Bracey, J. D., and Burch, R., *J. Catal.* **86**, 384 (1984); Orita, H., Naito, S., and Tamaru, K., *J. Phys. Chem.* **89**, 3066 (1985).
- Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).
- Meriaudeau, P., Dutel, J. F., Defaux, M., and Naccache, C., *Stud. Surf. Sci. Catal.* **11**, 95 (1981); Meriaudeau, P., Ellestad, O. H., Defaux, M., and Naccache, C., *J. Catal.* **75**, 243 (1982).
- Rieck, J. S., and Bell, A. T., *J. Catal.* **99**, 262 (1986).

- Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81**, 147 (1983); Resasco, D. E., and Haller, G. L., *J. Catal.* **82**, 279 (1986); Sadeghi, H. R., and Henrich, V. E., *J. Catal.* **87**, 279 (1985).
- Mori, T., Masuda, H., Imai, H., Miyamoto, A., Baba, S., and Murakami, Y., *J. Phys. Chem.* **86**, 2753 (1982); Mori, T., Masuda, H., Imai, H., Miyamoto, A., Hasebe, R., and Murakami, Y., *J. Phys. Chem.* **87**, 3648 (1983); Niizuma, H., Hattori, T., Mori, T., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **87**, 3652 (1983); Mori, T., Miyamoto, A., Niizuma, H., Takahashi, N., Hattori, T., and Murakami, Y., *J. Phys. Chem.* **90**, 109 (1986); Mori, T., Miyamoto, A., Takahashi, N., Fukagaya, M., Hattori, T., and Murakami, Y., *J. Phys. Chem.* **90**, 5197 (1986); Mori, T., Masuda, H., Imai, H., Miyamoto, A., Niizuma, H., Hattori, T., and Murakami, Y., *J. Mol. Catal.* **25**, 263 (1984); Takahashi, N., Mori, T., Miyamoto, A., Hattori, T., and Murakami, Y., *Appl. Catal.* **22**, 137 (1986); Mori, T., Miyamoto, A., Takahashi, N., Niizuma, H., Hattori, T., and Murakami, Y., *J. Catal.* **102**, 199 (1986).
- Mori, T., Masuda, H., Imai, H., Taniguchi, S., Miyamoto, A., Hattori, T., and Murakami, Y., *J. Chem. Soc. Chem. Commun.*, 1244 (1986).
- Taniguchi, S., Mori, T., Mori, Y., Hattori, T., and Murakami, Y., in preparation.

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