High Activity of Strong Metal–Support Interaction Catalysts for Carbon Monoxide Hydrogenation revealed by Pulse Surface Reaction Rate Analysis

Toshiaki Mori,*[a] Hiroyuki Masuda,[a] Hisao Imai,[a] Shigeyoshi Taniguchi,[c] Akira Miyamoto,[b] Tadashi Hattori,[c] and Yuichi Murakami[c]

[a] *Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-Ku, Nagoya 462, Japan*
[b] *Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan*
[c] *Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan*

By use of pulse surface reaction rate analysis, it was found that the active sites on titania-supported Pt and Pd catalysts for methanation were much more active in the strong metal–support interaction state than in the normal state.

Some metal catalysts supported on reducible transition metal oxides such as TiO_2 or Nb_2O_5 show unique adsorption properties. On high temperature reduction (usually >723 K) they lose much of their ability for chemisorption of H_2 or CO. However, the chemisorption ability thus lost can to a large extent be restored on heating the catalyst in an O_2 atmosphere followed by low temperature reduction. This phenomenon is considered to result from a strong metal–support interaction (S.M.S.I.), but not from sintering of the supported metal.[1] Because of the marked reduction in chemisorptive ability, it is reasonable to assume that reactions in which hydrogen is concerned may be suppressed on the catalyst in the S.M.S.I. state. For the hydrogenation of benzene[2] or the hydrogenolysis of some hydrocarbons[3] this is found to be the case. Therefore, recent reports that titania-supported Ni, Pd, and Pt catalysts in their S.M.S.I. state have extremely large turnover frequencies for the hydrogenation of CO are surprising.[4] Although metals supported on TiO_2 exhibit higher activity for the hydrogenation of CO than on other oxide supports,[3,5] it is still uncertain why the S.M.S.I. catalysts are more active than the normal catalysts; there is uncertainty over the number of active sites on S.M.S.I. catalysts.

We have developed the pulse surface reaction rate analysis (P.S.R.A.) technique and demonstrated its applicability for CO hydrogenation.[6,7] In this method, because the rate is measured for the process with exclusion of the adsorption step, the rate constant on each functioning active site on the catalyst can be determined directly without any information about the number of active sites. It is, therefore, of relevance to investigate the catalytic properties of S.M.S.I. catalysts by P.S.R.A. The purpose of the present study is to determine the rate constant for methanation per active site on S.M.S.I.

Table 1. Amount of CO adsorbed and the rate constant per active site determined by P.S.R.A. for methanation on titania-supported Pt and Pd catalysts at 498 K.

	CO adsorbed/ µmol g^{-1}		Rate constant, k/s^{-1}	
Pretreatment[a]	Pt	Pd	Pt	Pd
(A)	33.4	38.0	33.7	32.3
(B)	1.85	1.09	317	205
(C)	17.9	23.0	46.9	55.0

[a] (A): heated in flowing O_2 at 723 K for 2 h, followed by reduction at 523 K for 2 h; (B): after (A), reduced at 773 K for 1 h; (C): after (B), heated in flowing O_2 at 723 K for 2 h, followed by reduction at 523 K for 2 h.

catalysts and to examine whether or not the 'real' activity of S.M.S.I. catalysts is different from that in the normal state.

Catalysts were prepared by impregnating TiO_2 (Nippon Aerosil, P-25) with an aqueous solution containing Pt or Pd ions, followed by drying.† The metal loadings were 1.0 wt%. Before use, they were heated in flowing O_2 at 723 K for 2 h and then reduced in flowing H_2 at 523 K for 2 h. The S.M.S.I. catalysts were obtained by reduction at 773 K for 1 h. After the rate measurements, the S.M.S.I. catalysts were heated in flowing O_2 at 723 K for 1 h and then reduced in flowing H_2 at 523 K for 2 h. The amount of CO adsorbed on the catalyst was determined by a conventional pulse adsorption method[8] at room temperature after the rate measurements for the catalyst with the above-mentioned pretreatments.

The P.S.R.A. experiments were carried out as described previously.[6] On introducing a small amount of CO onto a catalyst *via* H_2 carrier gas, it is immediately adsorbed, and then gradual hydrogenation to produce CH_4 takes place, the dynamics of which give the rate constant per active site on the catalyst.

Table 1 shows the results of rate and adsorption measurements for the titania-supported Pt and Pd catalysts. After low temperature reduction (at 523 K), both catalysts adsorbed a considerable amount of CO. However, when the catalysts were subjected to subsequent high temperature reduction at 773 K, the amount of adsorbed CO drastically decreased to about 1/20th of the original amount. When the catalyst which had already lost its chemisorption ability was heated in flowing O_2 followed by low temperature reduction, the chemisorption ability was to a large extent restored. This indicates that the drastic decrease in the amount of adsorbed CO results primarily from S.M.S.I. and that sintering of the supported metal in the catalyst is a minor cause.

It is interesting that the rate constant per active site determined for methanation by P.S.R.A. depends on the pretreatment. After high temperature reduction of the titania-supported catalysts, which changes them into the S.M.S.I. state, the rate constants greatly increase; *i.e.*, rate constants for the Pt and Pd catalysts are about ten and seven times larger, respectively, in the S.M.S.I. state than in the normal state. However, when the S.M.S.I. catalysts were heated in flowing O_2, followed by low temperature reduction, the rate constants were almost the same as those in the normal state. Because in the present P.S.R.A. experiments the rate constant for methanation can directly be determined for each active site on the catalyst, the results in Table 1 clearly indicate that the intrinsic activity of the individual active sites on the titania-supported Pt and Pd catalysts greatly increases in the S.M.S.I. state.

The origin of the high activity of the S.M.S.I. catalyst for methanation is being investigated.

Received, 13th May 1986; Com. 640

References

1 S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.

2 P. Meriaudeau, J. F. Dutel, M. Defaux, and C. Naccache, *Stud. Surf. Sci. Catal.*, 1982, **11**, 95.

3 R. Burch and A. R. Flambard, *J. Catal.*, 1982, **78**, 389.

4 M. A. Vannice and R. L. Garten, *J. Catal.*, 1978, **56**, 236; S-Y. Wang, S. H. Moon, and M. A. Vannice, *ibid.*, 1981, **71**, 167; M. A. Vannice and C. C. Twu, *ibid.*, 1983, **82**, 213.

5 M. A. Vannice and C. Sudhakar, *J. Phys. Soc.*, 1984, **88**, 2429.

6 T. Mori, H. Masuda, H. Imai, A. Miyamoto, S. Baba, and Y. Murakami, *J. Phys. Chem.*, 1982, **86**, 2753; T. Mori, H. Masuda, H. Imai, A. Miyamoto, R. Hasebe, and Y. Murakami, *ibid.*, 1983, **87**, 3648; T. Mori, H. Masuda, H. Imai, A. Miyamoto, H. Niizuma, T. Hattori, and Y. Murakami, *J. Mol. Catal.*, 1984, **25**, 263.

7 T. Mori, A. Miyamoto, N. Niizuma, N. Takahashi, T. Hattori, and Y. Murakami, *J. Phys. Chem.*, 1986, **90**, 109.

8 Y. Murakami, in 'Preparation of Catalysts III,' eds. G. Poncelet, P. Grange, and P. A. Jacobs, Elsevier, Amsterdam, 1983, p. 775.

---

† The precursors of the supported Pt and Pd metals were aqueous solutions of H_2PtCl_6 and $PdCl_2$, the metal contents of which were 15.4 and 15.3 wt%, respectively. They were obtained commercially from Tanaka Kikinzoko Kogyo.