JOURNAL OF CATALYSIS **116**, 108–118 (1989)

# Effect of Strong Metal–Support Interaction on the Rate of Hydrogenation of Adsorbed Carbon Monoxide over Titania-Supported Noble Metal Catalysts As Revealed by Pulse Surface Reaction Rate Analysis

SHIGEYOSHI TANIGUCHI, TOSHIAKI MORI,[1],* YOSHIHIKO MORI, TADASHI HATTORI, AND YUICHI MURAKAMI

*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, and *Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan*

Received July 6, 1988; revised October 19, 1988

On the basis of the rate constant per active site determined by pulse surface reaction rate analysis (PSRA), the effect of the strong metal–support interaction (SMSI) on the hydrogenation of adsorbed CO was studied for titania-supported noble metal catalysts. Reduction at 773 K resulted in a drastic decrease in the amount of CO adsorbed on all noble metals examined. The observed suppression of CO chemisorption resulted mainly from SMSI, because the chemisorption ability was restored considerably by heating these catalysts in an $O_2$ atmosphere and then reducing at 523 K. It was found that the effect of SMSI on the hydrogenation of adsorbed CO was different from one noble metal to another, although its effect on CO chemisorption was common to all titania-supported noble metals. Pt and Pd exhibited a much higher hydrogenation activity in their SMSI state than in their normal state, whereas Rh, Ru, and Ir exhibited almost the same activity in both states. By heating titania-supported Pt and Pd in $O_2$ and then reducing at 523 K, concomitant with destruction of the SMSI state, the high hydrogenation activity disappeared to near each original value. Subsequent reduction at 773 K again brought these catalysts to the SMSI state, accompanied by an increase in their activity. From these results, a possible cause is discussed for the high activity on Pt and Pd in the SMSI state and for its absence on Rh, Ru, and Ir in the SMSI state.

## INTRODUCTION

Among the stimulating problems in heterogeneous catalysis, the strong metal–support interaction (SMSI) has received much attention (*1–3*). After high-temperature reduction (HTR), most metals supported on a reducible oxide like titania lose a large part of their chemisorption ability for $H_2$ and CO. However, when the catalyst that has lost the chemisorption ability is heated in an $O_2$ atmosphere and subjected to low-temperature reduction (LTR), the chemisorption ability is almost completely restored. The drastic suppression in the chemisorption ability caused by HTR was ascribed by Tauster *et al.* to SMSI, but not to sintering of the supported metal (*4*). As a plausible model for SMSI, it has been proposed that titania suboxide ($TiO_x$, $1 < x < 2$) species, formed by HTR, migrate onto the surface of the metal particles, by which the adsorption sites on the catalyst are blocked (*5–8*).

Owing to the great loss of the chemisorption ability for $H_2$ or CO, it is quite reasonable to assume that a titania-supported catalyst in the SMSI state exhibits a low activity for reactions in which hydrogen atoms are concerned. In fact, for hydrogenation of benzene (*9*) or hydrogenolysis of some hydrocarbons (*5, 7, 9–12*), this is found to be the case. Relative to these reactions, the situation for CO hydrogenation or methanation on titania-supported metal catalysts seems to be different. In this reaction, Vannice and his co-workers reported

---

[1] To whom all correspondence should be addressed.

0021-9517/89 $3.00

an extremely large turnover frequency (TOF) for titania-supported Ni, Pd, and Pt in their SMSI state (*13–15*). It was also found that titania-covered Pt (*16*) and Rh (*17*) foils, being models for the SMSI catalyst, exhibited an enhanced activity and kinetics different from those on uncovered metal foils. Burch and his co-workers, on the other hand, reported that the high specific methanation activity is due to the support effect of $TiO_2$, but not to SMSI (*9, 12*).

Previous studies revealed an interesting property of the SMSI catalyst. It should, however, be recollected that TOF or the specific activity is the activity normalized by the number of adsorption sites but not by the number of active sites on the altered catalyst. Furthermore, there is an additional serious problem in examining the high methanation activity of the SMSI catalyst: the SMSI state can be destroyed by the $H_2O$ produced during the methanation (*18, 19*). The high methanation activity of the SMSI catalyst should, therefore, be examined in terms of the activity concerning the active site and also under conditions unaffected by the $H_2O$ produced. Recently, Rieck and Bell qualitatively confirmed by using temperature-programmed surface reaction, which satisfies one of the conditions described above, that the methanation activity of $SiO_2$- and $TiO_2$-supported Pd catalysts was increased by $TiO_x$ moieties that had migrated onto the Pd metal particles (*20*).

We have developed the pulse surface reaction rate analysis (PSRA) technique to determine the rate constant per active site on the catalyst and have demonstrated its applicability to CO hydrogenation (*21–24*). A marked difference is present in the rate analysis between PSRA and conventional methods: in the former method, only adsorbed CO is considered as initial reacting species for CO hydrogenation, except $H_2$, whereas gaseous CO and adsorption sites are considered in the latter method. This is the reason why PSRA can determine the rate constant per active site without any information about the number of active sites and why the rate measured by the conventional method is not free from the number of adsorption sites. PSRA has a further advantage: the rate for the initial state of the catalyst can be measured with minimal influence of $H_2O$ produced. It is, therefore, relevant to reveal the catalytic properties of the SMSI catalysts by using PSRA. In the present study, on the basis of the rate constant per active site determined by PSRA, the effect of SMSI on the hydrogenation of adsorbed CO was studied over titania-supported noble metal catalysts.

## EXPERIMENTAL

Titania-supported noble metal catalysts (metal loading 1.0 wt%, unless otherwise specified) were prepared by impregnating $TiO_2$ (Nippon Aerosil, P-25) with an aqueous solution of the respective noble metal chloride ($RuCl_3$, $RhCl_3$, $PdCl_2$, $IrCl_4$, or $H_2PtCl_6$), followed by drying overnight at 383 K. After the catalyst was heated in an $O_2$ stream at 723 K for 2 h, it was reduced with $H_2$ at 523 K and subsequently reduced at elevated temperatures for 1 h, followed by rate measurement. The catalyst, which had been reduced at 773 K for 1 h, was heated in flowing $O_2$ at 723 K for 1 h and then reduced at 523 K for 2 h. In the present paper, HTR and LTR were at 773 and 523 K, respectively. After each rate measurement, the amount of CO adsorbed on the catalyst at 298 K was determined by a conventional pulse adsorption method using He as a carrier gas. Some catalysts were examined in a JEOL JEM-200CX transmission electron microscope.

In the hydrogenation of adsorbed CO, the rate constant per active site was determined by use of PSRA in a manner described elsewhere (*21–24*). The PSRA apparatus is a pulse microreactor. To minimize the dispersion of gases eluted from a catalyst bed, the outlet of the reactor was directly connected to the inlet of a flame ionization detector (FID) without any separation column. Since $CH_4$ is the sole product among hydrocarbons under the conditions of PSRA experiments, the FID can monitor the $CH_4$ response without any disturbance by the unreacted CO or the $H_2O$ produced.

## RESULTS

### *Chemisorption Measurements for Supported Noble Metal Catalysts*

CO chemisorption was measured and the results are summarized in Table 1. HTR caused a drastic decrease in the amount of CO adsorbed on all titania-supported noble metals. This agrees with published results, where the suppression of CO chemisorption after HTR is ascribed to SMSI (*1–8*). Sintering of the supported metal is another possible cause of the decrease in the amount of CO adsorption. It seems, however, that the observed suppression in CO chemisorption is too pronounced to be ascribed primarily to sintering of the supported metal. To confirm this, electron micrographs were taken for titania-supported noble metal catalysts. Figures 1 and 2 show typical results for 1 wt% Pt and 2.2 wt% Rh. Irrespective of reduction temperatures, very small particles of a noble metal (particle size, <2 nm for Pt and <3 nm for Rh), the size of which agreed with that determined from CO chemisorption after LTR, were dispersed on large particles of titania. There was no reliable evidence for the change in both the size and the shape of metal particles between LTR and HTR, in accordance with the literature (*25, 26*). These indicate that the suppression of CO chemisorption after HTR does not result from sintering. As described below, the chemisorption ability was considerably restored after the heat treatment in $O_2$ followed by LTR, which indicates again that, as a main cause, SMSI is responsible for the suppression in CO chemisorption on titania-supported noble metal catalysts.

### *Rate Constant for the Hydrogenation of Adsorbed CO Determined by PSRA*

When a small amount of CO (usually 10 $mm^3$) was pulsed via the $H_2$ carrier gas to a Pt catalyst at elevated temperatures (e.g., see Table 1), $CH_4$ was produced selectively. The amount of $CH_4$ produced after LTR was almost the same as that of pulsed CO, which indicates that the desorption of adsorbed CO is negligible under the condition of PSRA experiments. The chromatographic peak of the $CH_4$ produced showed a

TABLE 1

Amounts of CO Adsorbed on the Catalyst and Rate Constants for the Hydrogenation of Adsorbed CO after Low- and High-Temperature Reduction

| Metal[a] | Amount of CO adsorbed at 298 K ($\mu$mol $g^{-1}$) | | | Dispersion[b] (%) | Rate constant for hydrogenation at 498 K ($s^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | LTR | HTR | HTR/LTR | | LTR | HTR | HTR/LTR |
| Pt | 53.2 | 0.5 | 0.01 | 104 | 0.012 | 0.149 | 11.9 |
| Pd | 34.1 | 6.9 | 0.20 | 36 | 0.016 | 0.132 | 8.1 |
| Rh | 73.2 | 23.5 | 0.32 | 75 | 0.458 | 0.494 | 1.1 |
| Rh[c] | 114 | 12.5 | 0.11 | 53 | 0.226 | 0.305 | 1.3 |
| Ru | 12.8 | 2.9 | 0.22 | 13 | 0.470[d] | 0.390[d] | 0.8 |
| Ir | 15.2 | 0.3 | 0.02 | 29 | 0.226 | 0.158 | 0.7 |

[a] Metal loading, 1 wt%.

[b] Determined from the amount of CO adsorbed after LTR.

[c] Metal loading, 2.2 wt%; reaction temperature, 473 K.

[d] Reaction temperature, 453 K.

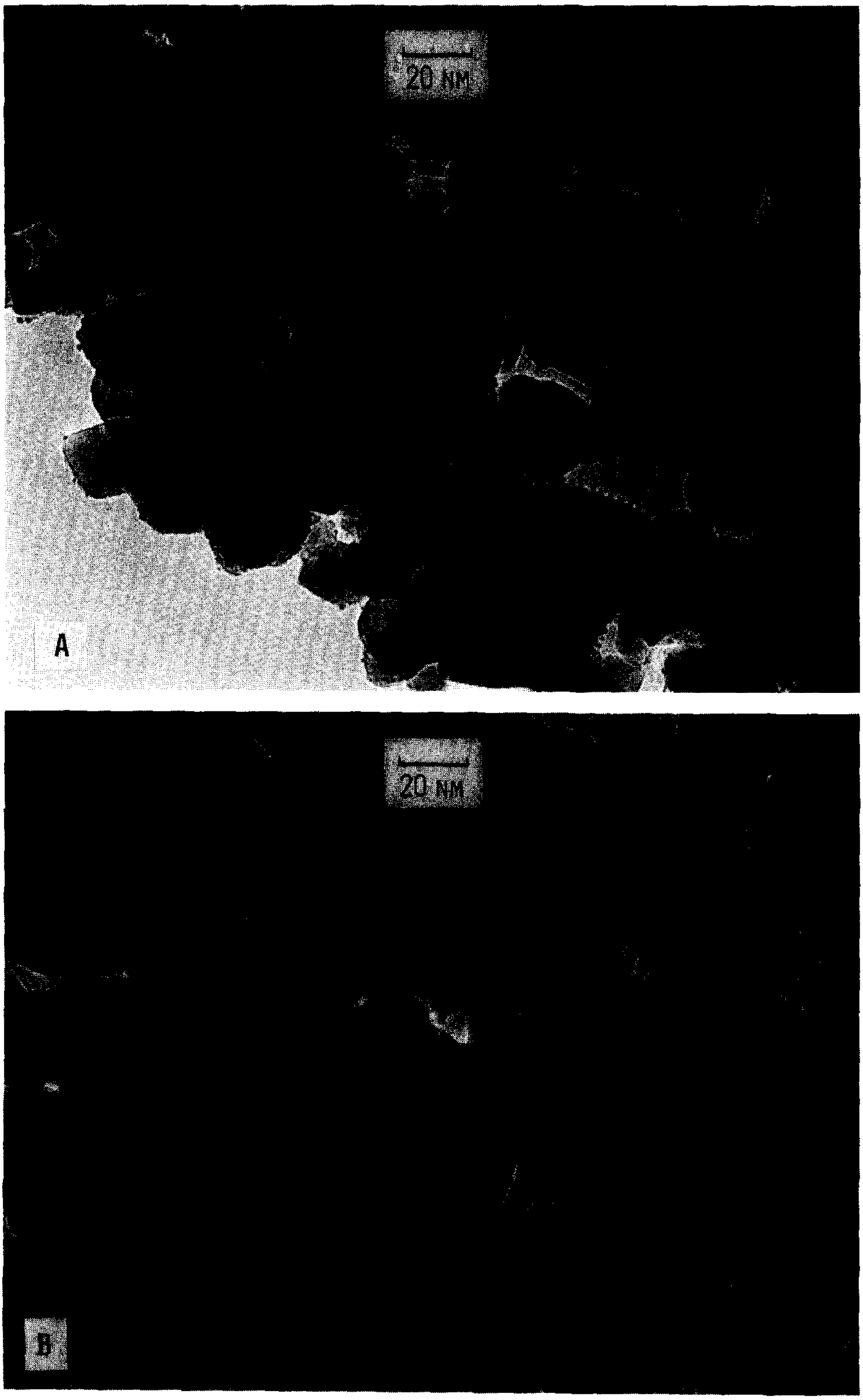

FIG. 1. Electron micrographs for Pt/$TiO_2$ after LTR (A) and after HTR (B).

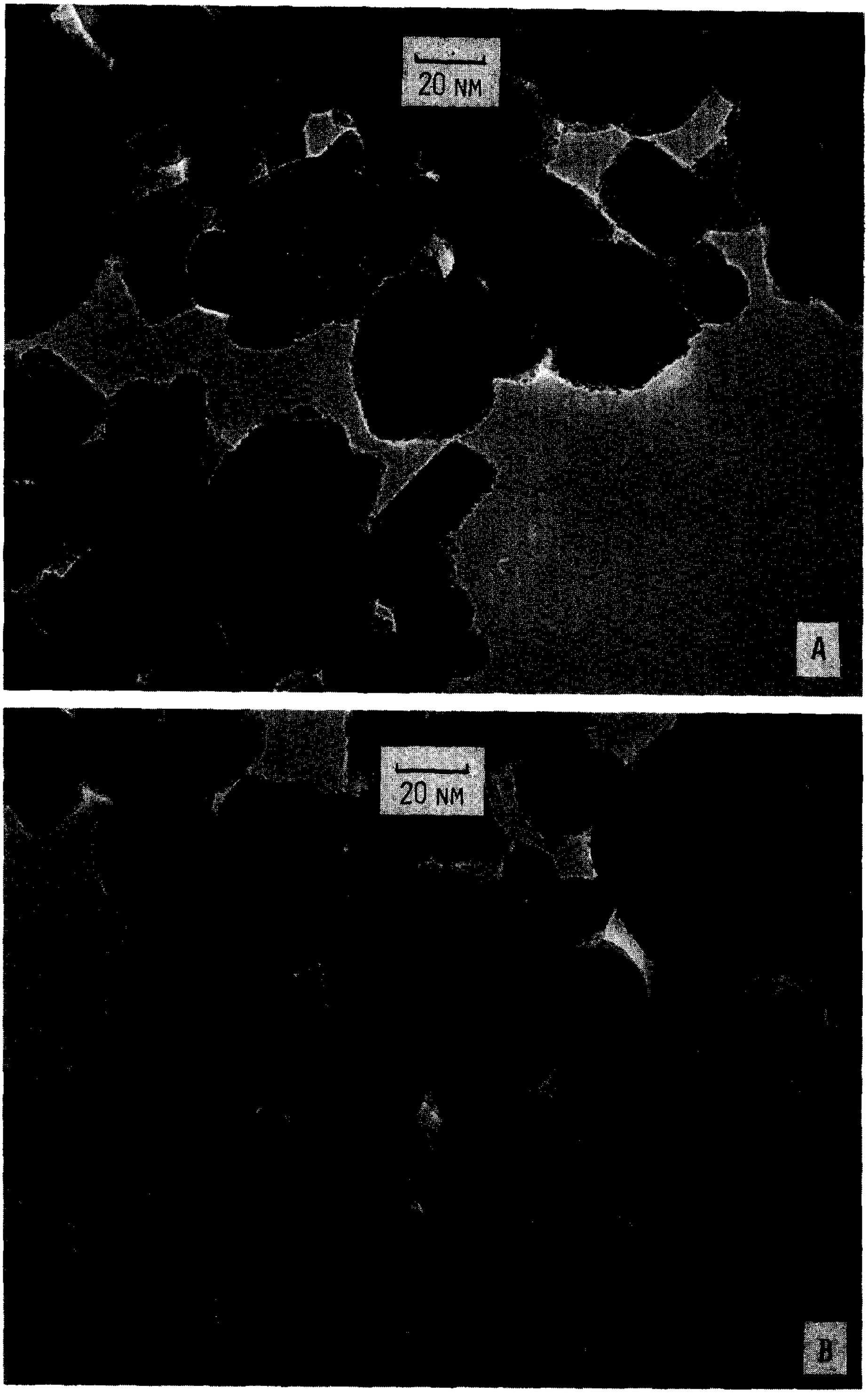

FIG. 2. Electron micrographs for Rh/TiO$_2$ (metal loading, 2.2 wt%) after LTR (A) and after HTR (B).

pronounced tailing after a steep rise, as typically shown in Fig. 3. These findings indicate that the pulsed CO is adsorbed immediately on the catalyst and then hydrogenated gradually with the $H_2$ carrier gas to produce $CH_4$. On Pt after HTR, a much more rapid decay of the $CH_4$ response can be observed, as shown by the broken line in Fig. 3. Assuming that the rate of $CH_4$ production or of the hydrogenation of adsorbed CO [$r(t)$] is first order with respect to the number of adsorbed CO molecules ($N_{CO}$),

$$r(t) = (dN_{CO}/dt) = k_H N_{CO} \qquad (1)$$

where $k_H$ is the first-order rate constant per active site. Integration of Eq. (1) leads to

$$\ln r(t) = \ln(k_H N^0_{CO}) - k_H t \qquad (2)$$

where $N^0_{CO}$ is $N_{CO}$ at $t = 0$. Equation (2) indicates that the relationship between ln $r(t)$ and time should give a straight line, the slope of which is the rate constant per active site (*21–24*).

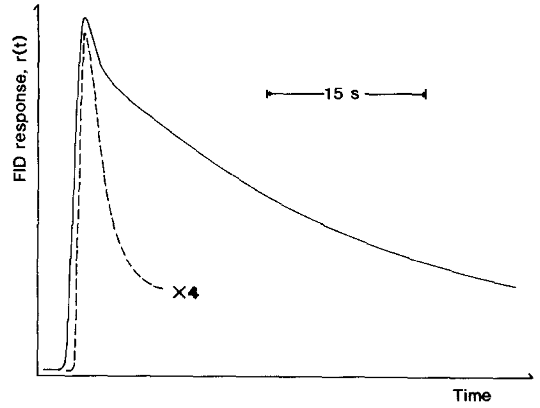

FIG. 3. Chromatographic peaks of $CH_4$ produced from the hydrogenation of adsorbed CO on $Pt/TiO_2$ catalyst in the normal state (solid line) and in their SMSI state (broken line). Catalyst weight, 100 mg; reaction temperature, 498 K; flow rate of carrier gas, 40 $cm^3$ $min^{-1}$; amount of CO pulsed, 10 $mm^3$.

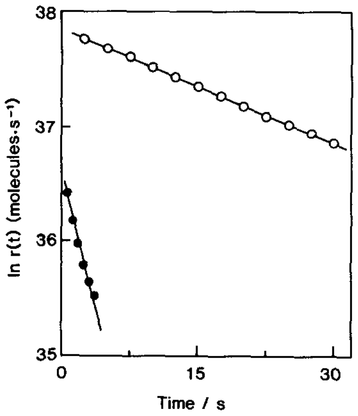

FIG. 4. Relationship between ln $r(t)$ and time for $Pt/TiO_2$ in the normal state (open circle) and in the SMSI state (filled circle). In these rate analyses, the time yielding the maximum reaction rate was tentatively set at zero.

Figure 4 shows the observed relationships between ln $r(t)$ and time. Good straight lines are obtained. For the pulse size below the saturation capacity of the catalyst, the slope of the straight line was independent of the amount of the CO pulse. Both findings, the linear relationship and the independence of the slope of the pulse size, satisfy the assumption of the first-order rate equation. When the amount of the CO pulse exceeded the saturation capacity, ln $r(t)$ versus time deviated from the linear relationship at the beginning of the decay curve in such a way that the slope became smaller, corresponding to the suppression of the hydrogenation of adsorbed CO. In the intermediate part of the decay curve, however, ln $r(t)$ versus time gave a straight line, the slope of which was almost the same as that for the small CO pulse. Consequently, the rate constant per active site on the catalyst can be determined from the slope of the observed linear relationship between ln $r(t)$ and time. In Fig. 4, the reaction rate is considerably smaller after HTR than after LTR, although the rate constant is very much larger after HTR than after LTR. This is very reasonable, because SMSI decreases the number of adsorption sites, thereby decreasing the rate [see Eq. (1)].

Table 1 summarizes the rate constants determined by PSRA for the hydrogenation of adsorbed CO. Relative to Rh, Ru, and Ir, both Pt and Pd exhibit low hydrogenation activity, the trend of which is in accord with TOFs reported in the literature (*27*). The striking feature in Table 1 is, however, that HTR caused a great increase in the rate constant on Pt and Pd, but not on Rh, Ru, and Ir. Because the rate constant determined by PSRA is not influenced by the number of active sites (*21–24*), the results in Table 1 indicate that HTR alters the nature of the active site on titania-supported Pt and Pd, while it does not on titania-supported Rh, Ru, and Ir. The absence of enhanced hydrogenation activity of the present titania-supported Rh seems to be in conflict with published results, where methanation was found to be enhanced on titania-covered Rh foils with appropriate amounts of $TiO_x$ (*17*). This may be due to the difference between our catalyst system and that in Ref. (*17*). Indeed, Orita *et al.* reported that conventional titania-supported Rh catalysts exhibited the lower conversion for CO hydrogenation in their SMSI state than in their normal state (*28*).

### *Effects of Reduction Temperature Both on CO Chemisorption and on Hydrogenation of Adsorbed CO*

The effects of the reduction temperature both on CO chemisorption and on the hydrogenation of adsorbed CO were more precisely investigated for titania-supported Pt, Pd, and Rh catalysts. The results are shown respectively in Figs. 5–7. As reduction temperature was increased to 773 K, the amount of CO adsorbed decreased to less than one-tenth of the original amount. The chemisorption ability was considerably restored by heating these catalysts in $O_2$ followed by LTR.

Relative to CO chemisorption, the hydrogenation activity varied with the reduction temperature in a different manner. The rate constants on titania-supported Pt varied little at reduction temperatures below 673 K, but it increased greatly at a reduction temperature of 723 K. The rate constant on titania-supported Pd did not change markedly at reduction temperatures below 723 K, but it increased greatly at a reduction temperature of 773 K. When Pt and Pd catalysts that had lost chemisorption ability and exhibited high hydrogenation activity were heated in $O_2$ followed by LTR, the rate constant decreased to near each original value. Compared to these two catalysts, the reduction temperature hardly influenced the hydrogenation activity of titania-supported Rh catalyst. Heating this catalyst in $O_2$ followed by LTR caused no marked change in

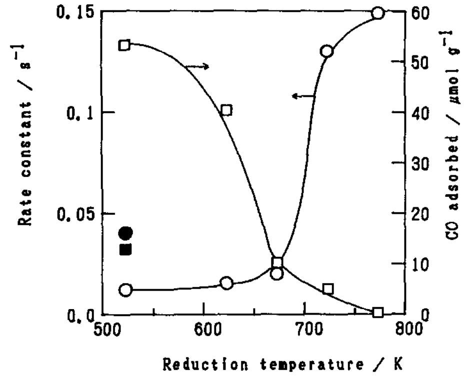

FIG. 5. Effects of the reduction temperature on the amount of CO adsorbed and on the rate constant for the hydrogenation of adsorbed CO at 498 K on Pt/$TiO_2$. The filled symbols represent the amount of adsorbed CO (square) and the rate constant (circle) determined after oxidation of the SMSI catalyst followed by reduction at 523 K.

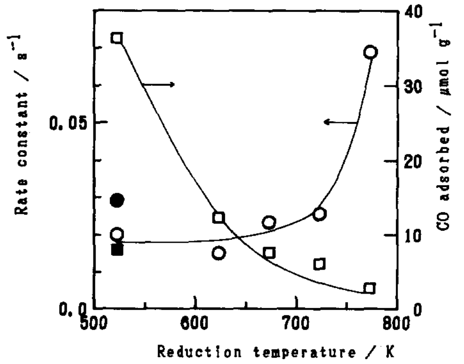

FIG. 6. Effects of the reduction temperature on the amount of CO adsorbed and on the rate constant for the hydrogenation of adsorbed CO at 498 K on Pd/$TiO_2$. For explanation of the filled symbols, see Fig. 5.

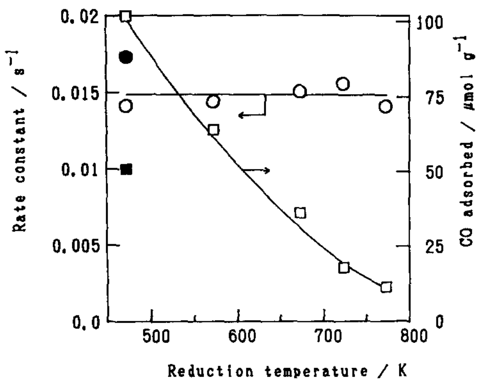

FIG. 7. Effects of the reduction temperature on the amount of CO adsorbed and on the rate constant for the hydrogenation of adsorbed CO at 423 K on Rh/$TiO_2$ (Rh loading, 2.2 wt%). For explanation of the filled symbols, see Fig. 5. After oxidation, the SMSI catalyst was reduced at 473 K, not at 523 K.

the hydrogenation activity. It is interesting to note in Figs. 5 and 6 that the reduction temperature at which the hydrogenation of adsorbed CO is greatly enhanced is considerably higher than the reduction temperature at which CO chemisorption is significantly suppressed.

### *Reversibility Both of the Suppression of CO Chemisorption and of the Enhanced Activity for the Hydrogenation of Adsorbed CO*

As described previously, HTR of titania-supported noble metals leads to the suppression of CO chemisorption, but their chemisorption ability is considerably restored by heating the catalyst in an $O_2$ atmosphere followed by LTR. However, the observed restoration seems to be inadequate; after the catalyst, having lost its chemisorption ability, was heated in $O_2$ followed by LTR, the amount of CO adsorbed was less than 50% of the original amount (see Figs. 5–7). Since, as described previously, sintering of the supported metal is negligible after HTR, it seems that the treatment in $O_2$ did not completely remove $TiO_x$ species from the metal surface, resulting in inadequate restoration.

Figure 8 shows results on the reversibility of the suppression in CO chemisorption and of the enhanced activity for the hydrogenation of adsorbed CO. As shown, both reversibilities are fairly good. Although the suppression of CO chemisorption caused by HTR is known not to be permanent, the enhanced activity for the hydrogenation of adsorbed CO is also not permanent, indicating that the active sites responsible for the increased hydrogenation activity disappear after the heat treatment in $O_2$ but are reproduced by the subsequent HTR.

## DISCUSSION

### *Applicability of PSRA to the SMSI System*

As illustrated in Fig. 3, the $CH_4$ response accompanies a pronounced tailing. Since desorption of adsorbed CO is negligible, the $CH_4$ response at a certain time is proportional to the reaction rate at this time. The decay of the $CH_4$ response or the decrease in the reaction rate is due to the decrease in the number of adsorbed CO molecules as a result of the hydrogenation. Therefore, as shown by Eq. (2), a plot of ln $r(t)$ versus time leads us to determine the rate constant per active site. When the amount of CO

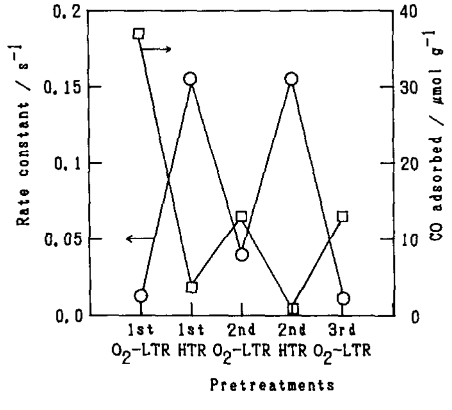

FIG. 8. Reversibility of SMSI in CO chemisorption and in the hydrogenation of adsorbed CO at 498 K on Pt/$TiO_2$. LTR, reduction at 523 K; HTR, reduction at 773 K; $O_2$-LTR, heating in an $O_2$ atmosphere at 723 K followed by reduction at 523 K.

pulsed is below the saturation capacity of the catalyst, the rate constant determined is independent of the amount of the CO pulse, which supports the validity of the present rate analysis. A large amount of the CO pulse should result in complete occupation of active sites, available for C–O bond dissociation, with adsorbed CO molecules. The complete occupation of active sites leads to suppression of the hydrogenation of adsorbed CO, which explains the deviation of the expected linear relationship between ln $r(t)$ and time at the beginning of the decay curve observed on pulsing CO with its excess amount. However, as soon as some adsorbed CO molecules are hydrogenated and thereby vacant sites are regenerated, the hydrogenation proceeds according to the first-order reaction, explaining the fact that the rate constant determined from the intermediate part of the decay curve is independent of the amount of the CO pulse. It seems, therefore, that the rate constant determined by PSRA is hardly influenced by the coverages of adsorbed CO molecules and hydrogen atoms and also the number of vacant sites.

### *Possible Explanation for the Difference in the Activity Variation between Pt or Pd and Rh, Ru, or Ir*

It is known that relative to an alumina- or silica-supported metal catalyst, a titania-supported metal exhibits high activity for CO hydrogenation even in the normal state after LTR (*9, 15, 29, 30*). Although the rate measured with PSRA is for the initial state of catalyst and not for the steady state, it was revealed that HTR further increased the rate constant per active site for titania-supported Pt and Pd, but not for titania-supported Rh, Ru, and Ir. For methanation, on the basis of TOF at steady state, Vannice and his co-workers also found the activity enhancement after HTR (*14, 15*). Since HTR brings our titania-supported Pt and Pd in the SMSI state, the increased activity after HTR results from SMSI. This conclusion is supported by the fact shown in Fig. 8 that the increased activity disappeared concomitantly with the destruction of the SMSI state of the catalyst. The high activity of the SMSI catalyst for CO hydrogenation has been attributed to newly formed active sites including titanium in a partially reduced state (*9, 12, 17, 31–33*). This idea may also explain the present activity increase on titania-supported Pt and Pd in their SMSI state observed on the basis of the rate constant per active site. In the normal state, pure surface metal sites are responsible for dissociation of the C–O bond. In the SMSI state, on the other hand, the titanium ions on the metal surface participate in C–O bond dissociation. The high activity of titania-supported Pt and Pd in their SMSI state results from the highly active metal–titanium ion sites. This occurs because due to the high affinity of these titanium ions for an oxygen atom, the active sites involving titanium ions in their reduced state are considered to be more active than the pure surface metal sites (*34*).

Despite the fact that HTR also brings titania-supported Rh, Ru, and Ir into the SMSI state and therefore the metal–titanium ion sites should also be formed on these catalysts in their SMSI state, an increased activity for the hydrogenation of adsorbed CO was not observed on titania-supported Rh, Ru, and Ir in their SMSI state. It is obvious that the variation in the morphology of these noble metals is not responsible for the absence of the increased activity, because, including Pt and Pd, HTR hardly changed the size and the shape of metal particles. The absence of the activity enhancement may, therefore, be explained by assuming that for C–O bond dissociation, the metal–titanium ion sites are more active than the Pt or Pd surface metal sites but less active than the Rh, Ru, or Ir surface metal sites. On Pt and Pd, the metal sites are responsible for C–O bond dissociation primarily in the normal state, whereas the more active metal–titanium ion sites are responsible for dissociation in the SMSI state, which leads to the increased activity of these two metals in their SMSI state. On Rh, Ru, and Ir, on the other hand, the metal sites are exclusively responsible for C–O bond dissociation in both states, because for these three noble metals, the metal sites are assumed to be more active than the sites involving titanium ions, which leads to the absence of an enhanced activity on titania-supported Rh, Ru, and Ir catalysts even in their SMSI state. Although the exact order of the catalytic activity for C–O bond dissociation is not known among noble metals, including the metal–titanium ion sites, the assumption mentioned above may be rationalized on the basis of the order of the hydrogenation activity of titania-supported noble metals in their normal state (see Table 1).

Other explanations are also possible for the difference in the effect of SMSI between the group of Pt and Pd and that of Rh, Ru, and Ir. The extent of the activation of adsorbed hydrogen or the ease of destroying SMSI by the $H_2O$ produced may, for example, be different between these two groups, resulting in other effects of SMSI for Rh, Ru, and Ir than for Pt and Pd. Further study is needed to clarify the difference.

It is likely that the active sites involving titanium ions formed on titania-supported Pt and Pd are activated for C–O bond dissociation at a reduction temperature higher than that at which the $TiO_x$ species migrate onto the metal surface. This may explain the difference observed in reduction temperature between suppression of CO chemisorption and enhancement in hydrogenation activity.

## CONCLUSION

From the rate measured by PSRA for the hydrogenation of adsorbed CO over titania-supported noble metal catalysts, it was found that the effect of SMSI on hydrogenation varied from one noble metal to another, though its effect on CO chemisorption was common to all noble metals. SMSI increased the rate constant per active site for Pt and Pd by about one order of magnitude, while it did not for Rh, Ru, and Ir. After heat treatment of titania-supported Pt and Pd in $O_2$ followed by LTR, concomitant with destruction of the SMSI state of these catalysts, the enhanced hydrogenation activity disappeared but appeared again after HTR. The enhanced hydrogenation activity for titania-supported Pt and Pd in their SMSI state and the absence of such enhancement for titania-supported Rh, Ru, and Ir, even in the SMSI state, are explained satisfactorily by the participation of titania suboxide species on the metal surface in C–O bond dissociation and the activity order among metal sites involving titanium ions.

## ACKNOWLEDGMENTS

The authors are grateful to Dr. Yoshio Murase of Government Industrial Research Institute, Nagoya, and Mr. Shin'ichi Komai of Nagoya University for taking electron micrographs.

## REFERENCES

1. Tauster, S. J., Fung. S. C., Baker, R. T. K., and Horsley, J. A. *Science* **211,** 4487 (1981).
2. Imelik, B., *et al.* (Eds.), "Studies in Surface Science and Catalysis," Vol. 11. Elsevier, Amsterdam, 1982.
3. Bond, G. C., and Burch, R., *in* "Catalysis (Specialist Periodical Reports)," Vol. 6. Chem. Soc., London, 1983.
4. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
5. Mériaudeau, P., Dutel, J. F., Defaux, M., and Naccache, C., *in* "Studies in Surface Science and Catalysis," Vol. 11, p. 95. Elsevier, Amsterdam, 1982.
6. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 147 (1983).
7. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
8. Sadeghi, H. R., and Henrich, V. E., *J. Catal.* **87,** 279 (1985).
9. Burch, R., and Flambard, A. R., *J. Catal.* **78,** 389 (1982).
10. Mériaudeau, P., Ellestad, O. H., Dufaux, M., and Naccache, C., *J. Catal.* **75,** 243 (1982).
11. Ko, E. I., Hupp, J. M., and Wagner, N. J., *J. Catal.* **86,** 315 (1984).
12. Bracey, J. D., and Burch, R., *J. Catal.* **86,** 384 (1984).
13. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).

*14.* Wang, S-Y., Moon, S. H., and Vannice, M. A., *J. Catal.* **71,** 167 (1981).

*15.* Vannice, M. A., and Twu, C. C., *J. Catal.* **82,** 213 (1983).

*16.* Demmin, R. A.,and Gorte, R. J., *J. Catal.* **105,** 373 (1987).

*17.* Levin, M. E., Salmeron, M., Bell, A. T., and Somorjai, G. A., *J. Catal.* **106,** 401 (1987).

*18.* Kunimori, K., Matsui, S., and Uchijima, T., *Chem. Lett.,* 359 (1985).

*19.* Anderson, J. B. F., and Burch, R., *Appl. Catal.* **21,** 179 (1986).

*20.* Rieck, J. S., and Bell, A. T., *J. Catal.* **99,** 262 (1986).

*21.* Mori, T., Masuda, H., Imai, H., Miyamoto, A., Baba, S., and Murakami, Y., *J. Phys. Chem.* **86,** 2753 (1982).

*22.* Mori, T., Masuda, H., Imai, H., Miyamoto, A., Hasebe, R., and Murakami, Y., *J. Phys. Chem.* **87,** 3648 (1983).

*23.* Niizuma, H., Hattori, T., Mori, T., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **87,** 3652 (1983).

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

*25.* Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979); **59,** 293 (1979).

*26.* Singh, A. K., Pande, N. K., and Bell, A. T., *J. Catal.* **94,** 422 (1985).

*27.* Vannice, M. A., *J. Catal.* **74,** 199 (1982).

*28.* Orita, H., Naito, S., and Tamaru, K., *J. Phys. Chem.* **89,** 3066 (1985).

*29.* Katzer, J. R., Sleight, A. W., Gajardo, P., Michel, J. B., Gleason, F., and McMillan, S., *Faraday Discuss.,* 121 (1981).

*30.* Solymosi, F., Tombácz, I., and Kocsis, M., *J. Catal.* **75,** 78 (1982).

*31.* Vannice, M. A., and Sudhakar, C., *J. Phys. Chem.* **88,** 2429 (1984).

*32.* Sachtler, W. M. H., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. V, p. 151. Verlag Chemie, Weinheim, 1984.

*33.* Rieck, J. S., and Bell, A. T., *J. Catal.* **96,** 88 (1985).

*34.* Ichikawa, M., Fukushima, T., and Shikakura, K., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 69. Verlag Chemie, Weinheim, 1984.