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Absence of the Enhanced Methanation Activity of Ni/TiO_2 in the SMSI State as Examined with Pulse Surface Reaction Rate Analysis

Toshiaki Mori,* Kenzi Suzuki, Masahiro Saito,†
Tadashi Hattori,†† and Yuichi Murakami††
Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462
†National Research Institute for Pollution and Resources, Yatabe-cho, Tsukuba 305
††Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464
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Synopsis. From rate measurements with pulse surface reaction rate analysis, it was found that the methanation activity of Ni/TiO_2 was the same both in the SMSI and in the normal states.

On high-temperature reduction (namely at 773 K), titania-supported metals exhibit an interesting phenomenon which is known as a strong metal-support interaction (SMSI).[1] As a result of SMSI, a large part of the chemisorption ability for H_2 or CO is lost without any agglomeration of a supported metal.[2] While most reactions in which hydrogen is involved are suppressed on the catalyst in the SMSI state, it has been found that the hydrogenation of CO or methanation is enhanced by SMSI.[3] This enhanced activity was measured on the basis of the turnover frequency (TOF), which is determined by dividing the rate by the number of adsorption sites. The suppression of chemisorption, however, makes it difficult to count precisely the number of adsorption sites. Indeed, there seems to be controversy over the enhanced activity of the SMSI catalyst for CO hydrogenation.[4]

Different from the conventional TOF, we have found that pulse surface reaction rate analysis (PSRA) is relevant in examining the activity enhancement of the SMSI catalyst for CO hydrogenation.[5] Since adsorbed CO is an initial reacting species under conditions of PSRA, the CO adsorption step is not involved in this rate analysis. Therefore, if the number of adsorbed CO molecules is decreased only by methanation, but not by desorption, we can determine directly the rate constant per active site without any information about the number of active sites from the analysis of the dynamic behavior of the adsorbed CO or the CH_4 produced.[6] PSRA has a further advantage: the rate for the initial state of a catalyst can be measured with minimal influence of the H_2O produced, which can destroy the SMSI state.[7] In the previous study, by using PSRA, we revealed that SMSI increased the activity for the hydrogenation of adsorbed CO on titania-supported Pt and Pd, but not on titania-supported Rh, Ru, and Ir.[5] Compared to noble metals, studies about the effect of SMSI on CO hydrogenation over titania-supported base metals are limited.[3,4] In the present study, selecting Ni as the base metal, we examined the effect of SMSI on the hydrogenation of adsorbed CO on the basis of the rate constant per active site determined by PSRA.

Experimental

Catalyst. Ni/TiO_2 catalyst (metal loading, 20 wt%) was prepared by impregnating TiO_2 (Nippon Aerosil, P-25) with an aqueous solution of $Ni(NO_3)_2$ followed by drying and subsequent calcination. Before making rate and chemisorption measurements, the catalyst was reduced at different temperatures for 4 h. In order to obtain information about the extents both of reduction and of sintering, X-ray powder diffraction measurements were made using a Shimadzu Cu *Kα* diffractometer (Shimadzu XD-3A).

Rate and Chemisorption Measurements. For the hydrogenation of adsorbed CO, the rate constant per active site was determined by PSRA in the manner described elsewhere.[5,6] The amount of CO chemisorbed on the catalyst was determined at 300 K using a conventional pulse adsorption apparatus.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns for

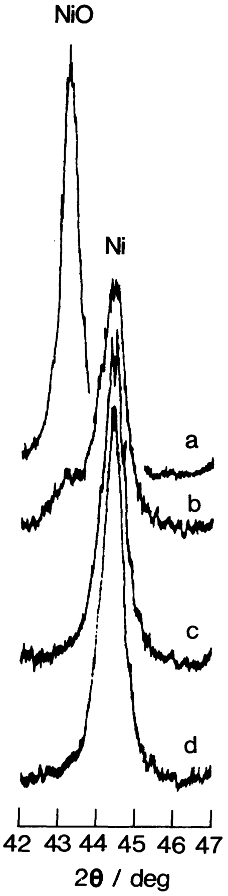

Fig. 1. X-Ray powder diffraction patterns for unreduced (a) and reduced Ni/TiO_2 catalysts. Reduction temperature: 573 K (b), 673 K (c), and 773 K (d).

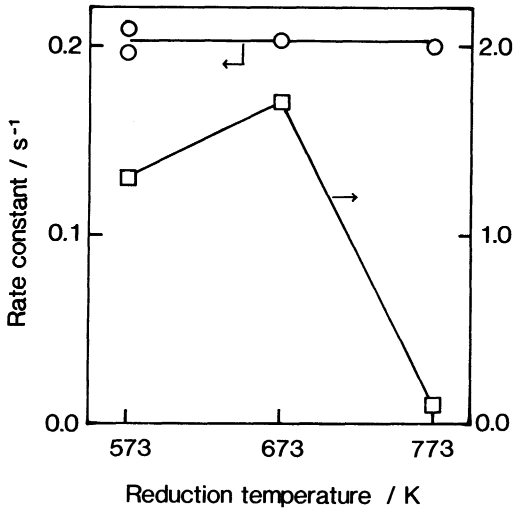

Fig. 2. Amount of CO adsorbed (□) and the rate constant per active site (○) on Ni/TiO_2 against the reduction temperature. Catalyst weight; 100 mg, reaction temperature; 453 K, flow rate of carrier gas; 40 cm^3 min^{-1}, amount of CO pulsed; 10 mm^3.

unreduced and reduced catalysts. Although most NiO is changed into Ni metal after reduction at 573 K, some of the NiO still remains unreduced. After reduction both at 673 and at 773 K, on the other hand, the NiO diffraction peak disappears, implying that complete reduction occurs. It is furthermore observable from X-ray diffraction patterns that the peak width at half height is almost the same at all reduction temperatures examined. This suggests that the particle size is hardly altered after reduction below 773 K.

The amount of CO adsorbed is shown in Fig. 2 as a function of the reduction temperature. A considerable amount of CO is adsorbed on the catalyst after reduction at 573 and 673 K, although the amount is smaller on reduction at 573 K than at 673 K. The lower amount of CO chemisorption on reduction at 573 K is ascribable to the incomplete reduction, as the X-ray diffraction shows (see Fig. 1). Contrary to this, CO chemisorption is suppressed almost completely after reduction at 773 K. Since reduction at 773 K did not cause the agglomeration of supported Ni metal particles, as described above, the drastic suppression of CO chemisorption should be attributed to SMSI.

Under experimental conditions of PSRA, a small amount of CO (usually 10 mm^3) pulsed via the H_2 carrier gas was immediately adsorbed on the catalyst and then hydrogenated selectively to CH_4. Analysis of the dynamics of the CH_4 produced permits us to determine the rate constant per active site.[5,6] The rate constant determined is also shown in Fig. 2 as a function of the reduction temperature. The rate constant is almost constant irrespective of the reduction temperature. Taking into account the fact that reduction at 773 K induces the SMSI state in the Ni/TiO_2, the results in Fig. 2 clearly indicates that the SMSI of this catalyst does not increase the rate constant per active site for the hydrogenation of adsorbed CO. It is interesting to compare the present results with the one previously obtained on noble metals.[5] Titania-supported Ni is very similar to titania-supported Rh, Ru, and Ir in a sense that their SMSI does not increase the activity for the hydrogenation of adsorbed CO.

It is now accepted that SMSI results from migration of TiO_x-suboxide species, formed by high-temperature reduction, onto the metal particles.[8] The suppression of CO chemisorption results from site blocking by the migrated TiO_x-suboxide, by which the number of adsorption sites is decreased. The influence of SMSI on CO hydrogenation has been attributed to this TiO_x-suboxide.[9] The suboxide takes part in C–O bond dissociation by bond formation between a titanium ion in a partially reduced state and an oxygen end of an adsorbed CO species. Due to the high affinity of the titanium ion in the reduced state for an oxygen atom, a C–O bond is readily dissociated, leading to an increase in the activity for CO hydrogenation. Since our Ni/TiO_2 is in the SMSI state after reduction at 773 K, the TiO_x-suboxide should be present on Ni metal particles. Nevertheless, this suboxide did not increase the activity for the hydrogenation of adsorbed CO. We have previously presented a possible explanation for the effect of the TiO_x-suboxide: the suboxide effectively takes part in the C–O bond dissociation on such a metal as Pt or Pd exhibiting a relatively low activity for CO hydrogenation. However, it does not work on a metal with high activity like Rh or Ru.[5] This may also explain the absence of the enhanced activity of Ni/TiO_2 in the SMSI state, because Ni is known to be one of the most active metals for CO hydrogenation.[10] This may again support our previous explanation.

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