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NOTE

Strong Metal–Oxide Interaction Induced by the Reduction of $NiTa_2O_6$ Supported on SiO_2

We have recently shown that ternary oxides of rhodium such as $RhNbO_4$, $RhVO_4$, and $MnRh_2O_4$ are formed almost exclusively on an SiO_2 support by mutual interaction between Rh and the oxides (niobia, etc.) during calcination treatment in O_2 or in air at high temperature (700–900°C) (1–3), and demonstrated that these ternary oxides (or the precursors) play important roles not only in the catalytic properties but also in the morphology changes of supported metal catalysts. The characteristic features of these ternary-oxide catalysts are as follows (1–9): (i) Rh metal is dispersed on SiO_2 after the decomposition of the ternary oxides by H_2 reduction; (ii) strong metal–oxide interactions are induced by H_2 reduction; (iii) the catalytic activity and selectivity can be controlled by the metal–oxide interactions; and (iv) regeneration of the ternary-oxide compounds can be achieved by calcination treatment.

Relatively few studies have been performed for the formation of other ternary-oxide systems such as nickel (e.g., $NiNb_2O_6$) (10, 11). The preparation method using citrate solutions (12, 13) has proved to be effective for the formation of an $NiNb_2O_6$ compound on an SiO_2 surface (11). This paper reports the formation of $NiTa_2O_6$ supported on SiO_2 by the citrate method. It is well known that the physical properties and structure of tantalum are very similar to those of niobium. However, tantalum oxide systems have recently attracted an interest because of the unique catalytic properties (14, 15) which are different from those of niobium oxide. In this work, the nature of metal–Ta_2O_5 interaction has been compared with that of metal–Nb_2O_5 interaction (11). The structure change of $NiTa_2O_6$ during the calcination and reduction treatments was studied by X-ray diffraction. The activity measurements of ethane hydrogenolysis were chosen as a test reaction (7, 16) to investigate the extent of the metal–oxide interaction after the decomposition of the $NiTa_2O_6$ compound by H_2 reduction.

Nickel citrate solution was prepared by dissolving hydrous $Ni(CH_3COO)_2$ in a 1.5 *M* (1 *M* = 1 mol dm^{-3}) citric acid, and aqueous tantalum oxalate solution was used to prepare a mixed citrate solution of nickel and tantalum in a separable flask (13). A calculated amount of SiO_2 (JRC-SIO-7) was added, and the system was evacuated and heated to evaporate the water at 60°C (12, 13). The thoroughly dried solid was calcined in air at high temperature (550–700°C) to obtain a $NiTa_2O_6/SiO_2$ catalyst. For comparison, a Ta_2O_5–Ni/SiO_2 catalyst was prepared by incipient wetness impregnation of aqueous solutions of $Ni(CH_3COO)_2$ and tantalum oxalate followed by the calcination treatment. The Ni content of the catalysts was 5.0 wt%, with an atomic tantalum-to-nickel ratio (Ta/Ni) of 2 or 4. X-ray diffraction (XRD) patterns of the catalysts after the calcination and/or reduction treatments were obtained with an X-ray diffractometer (Rigaku Co., Ltd.) equipped with a graphite monochromator for Cu$K\alpha$ (40 kV, 30 mA) radiation (6). The ethane hydrogenolysis activity was measured in a microcatalytic pulse reactor (4–7). Prior to each activity test, the sample in the reactor was treated in O_2 at 500°C for 1 h, followed by the H_2 reduction for 1 h at different temperatures (200–600°C) (4, 11).

Figure 1(1) shows the XRD patterns of the catalyst (Ta/Ni = 2) prepared by the citrate method. The broad background peak around 20° is due to the amorphous SiO_2 used as the support. After the calcination at 600°C, the diffraction peaks in Fig. 1(1) indicate essentially a single phase of columbite $NiTa_2O_6$ structure, as registered in JCPDS (13), although small peaks of NiO were also observed. So far as the authors are aware, no work has been performed for the preparation of $NiTa_2O_6$ supported on SiO_2. As shown in Fig. 1(2), when the Ta/Ni ratio was increased from 2 to 4, the intensities of the NiO peaks decreased significantly. Moreover, the peaks of $NiTa_2O_6$ became larger, which suggests that the formation of $NiTa_2O_6$ was more complete in the catalyst (Ta/Ni = 4).

Figure 2 shows the XRD patterns of the Ta_2O_5–Ni/SiO_2 catalyst prepared by the conventional impregnation method. In this case, no appreciable formation of $NiTa_2O_6$ was observed after calcination at 600°C. As shown in Fig. 2(2), the calcination at the higher temperature (700°C) resulted in the formation of mixed phases of $NiTa_2O_6$, Ta_2O_5, and NiO on SiO_2. This result suggests that more intimate mixing between Ni and Ta components and higher homogeneity were achieved by using the citrate solutions (chemical mixing method (13)).

Figures 3 and 4 show the H_2 reduction behavior of

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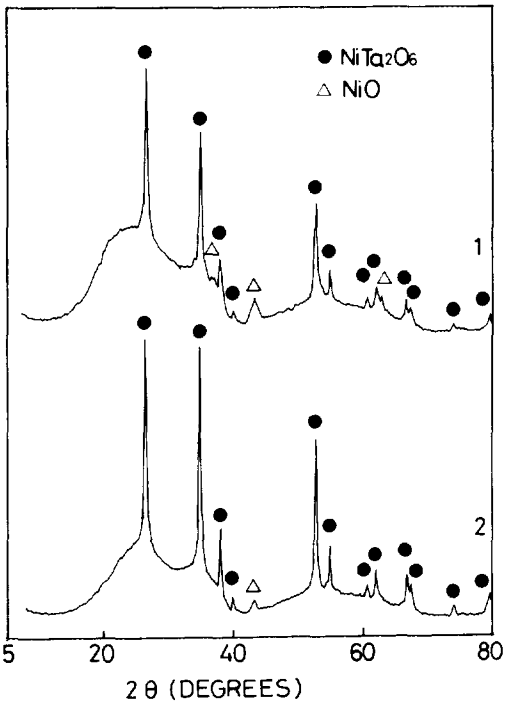

FIG. 1. X-ray diffraction patterns of the nickel tantalum oxide supported on SiO_2 prepared by the citrate method (calcined in air at 600°C): (1) Ta/Ni = 2 and (2) Ta/Ni = 4.

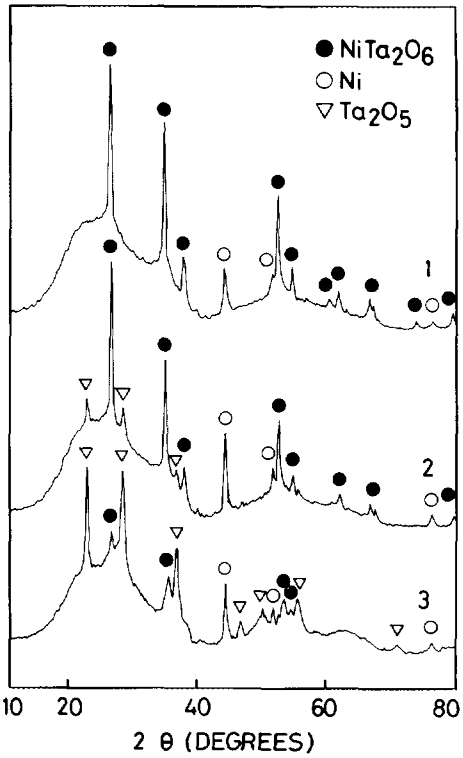

FIG. 3. X-ray diffraction patterns of the $NiTa_2O_6/SiO_2$ catalyst (Ta/Ni = 2) after H_2 treatment at (1) 500°C, (2) 600°C, and (3) 700°C.

$NiTa_2O_6$ on SiO_2. No reduction of the $NiTa_2O_6$ crystallite was observed after H_2 treatment at 500°C. Small parts of the $NiTa_2O_6$ crystallites may be reduced by H_2 treatment at 600°C, because the intensities of the $NiTa_2O_6$ peaks became smaller, as shown in Fig. 3(2) and Fig. 4(2). The decomposition of the $NiTa_2O_6$ compound was clearly observed by H_2 reduction at 700°C, as shown in Fig. 3(3) and Fig. 4(3). These results show that the $NiTa_2O_6$ compound is more tolerant in H_2 than the $NiNb_2O_6$ compound, the decomposition of which is initiated by H_2 reduction at 500°C (11). As also shown in Figs. 3 and 4, NiO was reduced to Ni metal by the H_2 treatment at 500 or at 600°C. The intensities of the Ni peaks were much smaller for the catalyst (Ta/Ni = 4). It should be noted that no big increase of the intensities of the Ni peaks was observed in Fig. 4(3), even though the $NiTa_2O_6$ was completely decomposed on SiO_2 by the reduction at 700°C. Highly dispersed Ni (which could not be detected by XRD method) was formed by the reduction of the $NiTa_2O_6$ compound. Redispersion of metal by the decomposition of such ternary-oxide compounds is one of the typical behaviors of the structural change during the oxidation–reduction treatments (1–9).

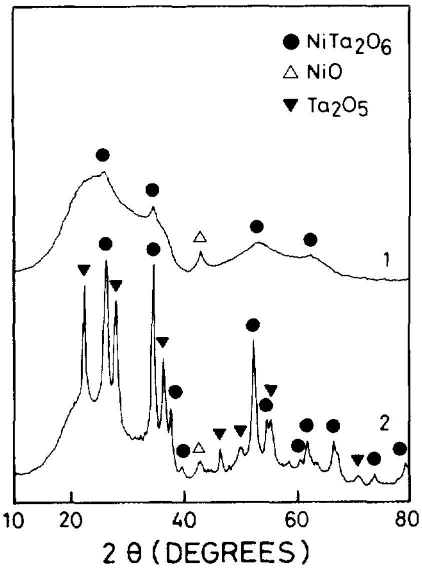

FIG. 2. X-ray diffraction patterns of the Ta_2O_5–Ni/SiO_2 catalyst prepared by the conventional impregnation method (Ta/Ni = 2) after calcination in air at (1) 600°C and (2) 700°C.

Figure 5 shows the ethane hydrogenolysis activities of the $NiTa_2O_6/SiO_2$ catalyst. In these measurements, the catalyst with the Ta/Ni ratio of four was chosen because the increase of the Ta/Ni ratio resulted in more complete formation of $NiTa_2O_6$ on SiO_2. The presence of excess NiO would not be acceptable for the activity measure-

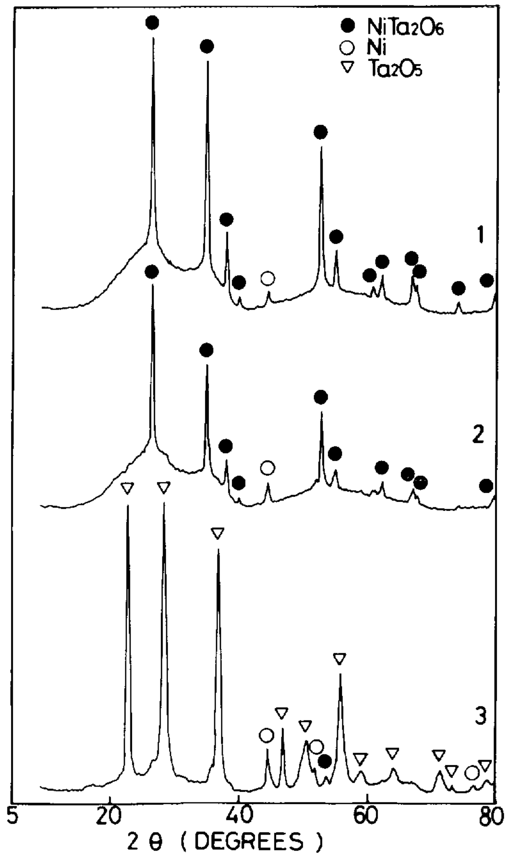

FIG. 4. X-ray diffraction patterns of the $NiTa_2O_6/SiO_2$ catalyst (Ta/Ni = 4) after H_2 treatment at (1) 500°C, (2) 600°C, and (3) 700°C.

ments of the $NiTa_2O_6/SiO_2$ catalyst, because NiO is reduced to Ni metal by H_2 treatment even at 400°C and Ni metal has a high activity for this reaction (11). In practice, for the catalyst (Ta/Ni = 4) there was no measurable activity of the ethane hydrogenolysis reaction within the range of reaction temperatures studied (up to 500°C (4)), unless the catalyst was treated in H_2 at 600°C or at the higher temperature (e.g., 700°C). This result suggests that the ethane hydrogenolysis activity of $NiTa_2O_6$ particles on SiO_2 is very low (the rate is less than 10^{-9} molecule/total Ni atom/s). Once the catalyst was reduced at 600°C, the catalyst showed some activities (Nos. 1 and 2 in Fig. 5) after the O_2 treatment at 500°C followed by low-temperature reduction (LTR) at 200 and 300°C. However, the activity decreased severely after high-temperature reduction (HTR) at 500 and 600°C (Nos. 3 and 4 in Fig. 5). After $NiTa_2O_6$ compound was decomposed by HTR at 700°C, the drastic change in the activity was observed again as the function of the H_2 reduction temperature (Nos. 5 to 8 in Fig. 5). These results demonstrate that a typical SMSI behavior (7, 16) is induced by the reduction of the $NiTa_2O_6/SiO_2$ catalyst.

It is interesting to note that the SMSI behavior was observed (Nos. 1 to 4 in Fig. 5) even though the $NiTa_2O_6$ particles on SiO_2 were not largely decomposed after HTR at 600°C (see Fig. 4(2)). The partial reduction of the $NiTa_2O_6$ particles may be sufficient to induce a strong metal–oxide (Ni–TaO_x) interaction. The degree of activity suppression after HTR at 600°C is more than four orders of magnitude, compared with that after LTR at 200°C. For the $NiNb_2O_6/SiO_2$ catalyst, the activity change was about three orders of magnitude between LTR at 200°C and HTR at 600°C (11, 17). Therefore, the extent of the metal–oxide (Ni–TaO_x) interaction appears to be stronger than that induced by the decomposition of the $NiNb_2O_6$ compound.

Summing up, a strong Ni–TaO_x interaction was formed by the reduction of $NiTa_2O_6$. The catalytic properties of such ternary oxides, as well as the chemical changes after

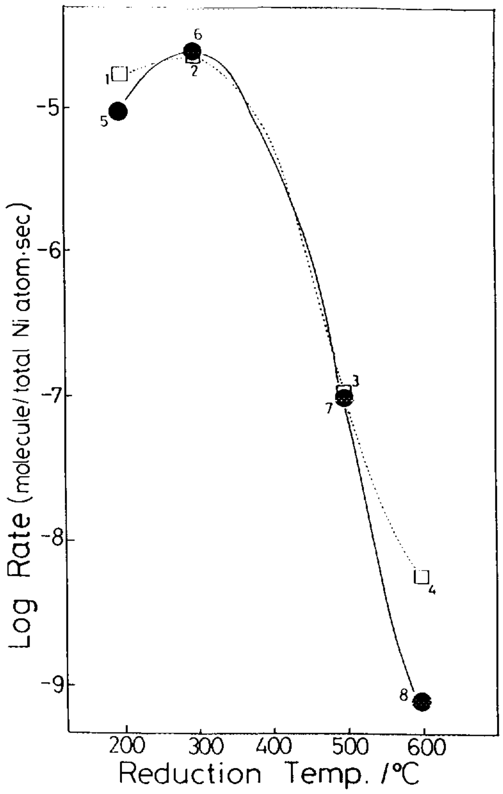

FIG. 5. Changes in the ethane hydrogenolysis activity (at 162°C) after the sequential oxidation–reduction treatments of the $NiTa_2O_6/SiO_2$ catalyst (Ta/Ni = 4): □, after the catalyst was treated in H_2 at 600°C, the activity measurements (Nos. 1 to 4) were performed; ●, after the catalyst was treated in H_2 at 700°C, the activity measurements (Nos. 5 to 8) were performed. Before each activity measurement, the catalyst was treated in O_2 at 500°C followed by H_2 treatment at the temperature shown in the x-axis in the figure.

the decomposition by H_2 reduction, deserve further attention.

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