Catalysis Letters 21 (1993) 283–290

Nickel–niobia interaction induced by the reduction of $NiNb_2O_6$ supported on SiO_2

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Received 3 April 1993; accepted 15 June 1993

Nickel niobate ($NiNb_2O_6$) supported on SiO_2 was prepared by a chemical mixing method using mixed Ni and Nb citrate solutions. X-ray diffraction study showed that the $NiNb_2O_6$ compound was reduced to Ni metal and NbO_2 after H_2 treatment at 600°C, and a strong Ni–niobia interaction was induced after the decomposition of the compound: the ethane hydrogenolysis activity was suppressed severely after high temperature reduction at 600°C, and recovered by O_2 treatment at 500°C followed by low-temperature reduction at 200°C. The selectivity of cyclohexane dehydrogenation was improved significantly by the Ni–niobia interaction, if compared with unpromoted Ni/SiO_2 catalyst, and the structural change and catalytic behaviors were compared with those of Rh double oxides such as $RhNbO_4$.

Keywords: Nickel niobate; $NiNb_2O_6$; ethane hydrogenolysis; dehydrogenation of cyclohexane; SMSI; metal–oxide interaction

1. Introduction

We have recently shown that rhodium niobate ($RhNbO_4$) is formed on SiO_2 support by mutual interaction between Rh and niobia during calcination treatment in O_2 or in air at high temperature (700–900°C) [1,2], and demonstrated that a typical strong metal–support interaction (SMSI) behavior appears when $RhNbO_4$ is reduced by hydrogen [2,3]. Moreover, such double-oxide compounds of Rh (e.g., $RhVO_4$, $MoRh_2O_6$, $MnRh_2O_4$ etc.) have been prepared intentionally on SiO_2 surface [4–6], and these catalyst systems have been used as starting materials to figure out the roles of metal–oxide interactions in catalysis (ethane hydrogenolysis and cyclohexane dehydrogenation reactions, etc.) of the supported metals after decomposition of the Rh compounds by H_2 reduction [7]. The characteristic features of these double-oxide catalysts are as follows [1–7]: (1) redispersion of the metal by H_2 reduction, (2) control of the catalytic activity and selectivity by metal–oxide

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interactions, and (3) regeneration of the double-oxide compounds by calcination treatment.

The same strategy may be applied to other double-oxide systems such as Ni (e.g., nickel niobate, etc.). Ko et al. [8,9] studied in detail Ni–niobia interaction in Nb_2O_5-supported and Nb_2O_5-modified Ni catalysts, which exhibit typical SMSI behavior [10], and the extent of the SMSI interaction has been studied from the activities of ethane hydrogenolysis (as a test reaction) [9]. However, no extensive study has been done for the formation of Ni niobate [11], which may play an important role in metal–oxide interaction in Nb_2O_5-modified Ni catalyst systems. In this work, Ni niobate ($NiNb_2O_6$) was prepared on SiO_2 support by a chemical mixing method using citrate solutions [12,13], and catalytic behavior of $NiNb_2O_6$ has been studied before and after the decomposition of the compound. This paper reports the structure change of $NiNb_2O_6$ during the calcination and reduction treatments, and the results of ethane hydrogenolysis and cyclohexane reactions are compared with those of unpromoted Ni/SiO_2 catalyst.

2. Experimental

A silica-supported Ni niobate catalyst was prepared from mixed citrate solutions of Ni and Nb, followed by vacuum-drying in the presence of SiO_2 (JRC-SIO-7) [12,13]. After drying at 120°C overnight, the sample was calcined in air at high temperatures (500–750°C). For a comparison, a niobia-promoted Ni/SiO_2 catalyst was prepared by incipient wetness impregnation of an aqueous solution of $(NH_4)_3[NbO(C_2O_4)_3]$ onto a Ni/SiO_2 catalyst (which had been reduced in H_2 at 500°C), followed by air calcination at 750°C. The Ni content of both catalysts was 5.0 wt%, with an atomic niobium-to-nickel ratio (Nb/Ni) of two.

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 Kα (40 kV, 30 Ma) radiation [2]. The catalytic activity measurements for ethane hydrogenolysis and cyclohexane reactions were performed in a microcatalytic pulse reactor [2–5]. Prior to each activity test, the sample in the reactor was heated in O_2 at 500°C for 1 h, followed by the H_2 reduction for 1 h at different temperatures (200–600°C).

3. Results and discussion

Fig. 1 shows the XRD patterns of the SiO_2-supported Ni niobate catalyst (Nb/Ni = 2) prepared by the citrate complexation method. The broad background peak around 20° is due to the amorphous SiO_2. After the calcination at 750°C, the diffraction pattern indicates essentially a single phase of columbite $NiNb_2O_6$ structure [13]. The formation of such Ni niobate on SiO_2 has been suggested on a niobia-

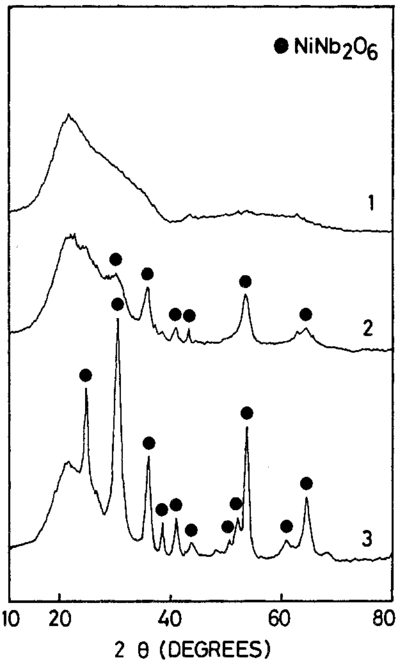

Fig. 1. X-ray diffraction patterns of the Ni niobate catalyst supported on SiO_2 calcined in air at (1) 500°C, (2) 600°C, and (3) 750°C.

modified Ni catalyst by selected-area diffraction using transmission electron microscopy [11]. When the Nb/Ni ratio was chosen to be unity, the presence of the excess NiO was observed in addition to the $NiNb_2O_6$ peaks [14]. Fig. 2 shows the XRD pattern of the Nb_2O_5-promoted Ni/SiO_2 catalyst prepared by the conven-

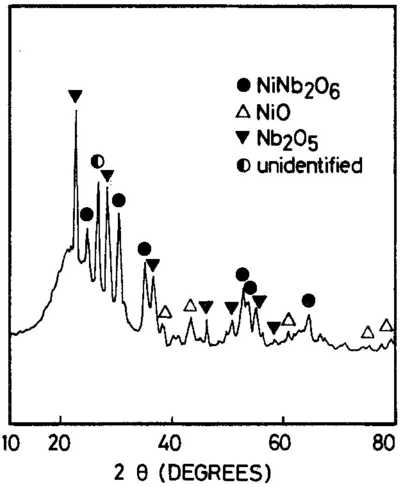

Fig. 2. X-ray diffraction pattern of the Nb_2O_5-promoted Ni/SiO_2 catalyst calcined in air at 750°C.

tional impregnation method. The calcination at 750°C resulted in the formation of three phases (NiO, Nb_2O_5 and $NiNb_2O_6$) on SiO_2. This result suggests that more intimate mixing between Ni and Nb components and higher homogeneity were achieved by using the citrate solutions (chemical mixing method [13]).

Fig. 3 shows the H_2 reduction behavior of $NiNb_2O_6$ on SiO_2. No reduction of the Ni niobate was observed after the H_2 treatment at 400°C. The decomposition of the $NiNb_2O_6$ compound was initiated by the H_2 reduction at 500°C, and finally reduced to Ni metal and NbO_2 in H_2 at 600°C, as shown in fig. 3 curve 3. For a comparison, the H_2 reduction behavior of nickel oxide (NiO) on SiO_2 is shown in fig. 4. The NiO was reduced partly to Ni metal at 400°C, and the reduction was complete after the H_2 treatment at 500°C. The $NiNb_2O_6$ compound is more tolerant in H_2 than the NiO on SiO_2.

Fig. 5 shows the ethane hydrogenolysis activities of the Ni niobate and NiO catalysts as a function of catalyst reduction temperature. For the $NiNb_2O_6/SiO_2$ catalyst, the catalytic activity was increased slightly with increasing reduction temperature to 300°C (No. 2), but decreased drastically after the decomposition of $NiNb_2O_6$ by high-temperature reduction (HTR) at 600°C (No. 4). The severe suppression in the hydrogenolysis activity after HTR is due to the covering of the Ni surface with NbO_x (probably, $x = 2$) (decoration model [10,15]), as shown in fig. 6.

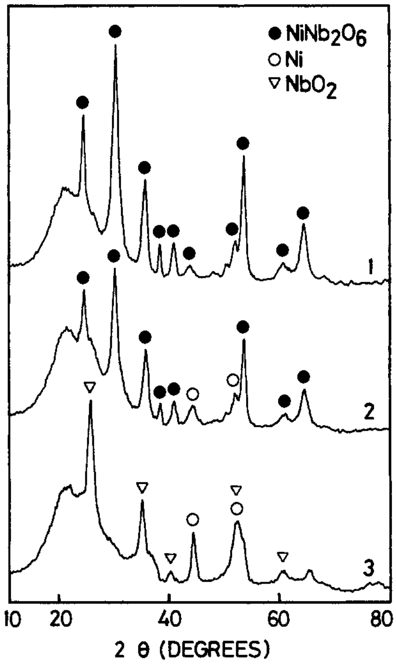

Fig. 3. X-ray diffraction patterns of the $NiNb_2O_6/SiO_2$ catalyst after the H_2 treatment at (1) 400°C, (2) 500°C, and (3) 600°C.

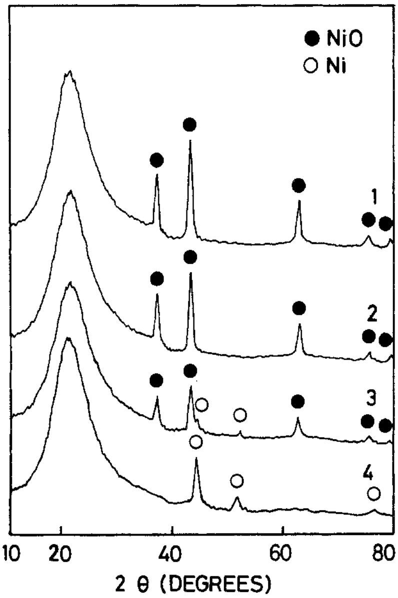

Fig. 4. X-ray diffraction patterns of the NiO/SiO_2 catalyst. (1) Calcination in air at 750°C; after (1), the catalyst was treated in H_2 at (2) 300°C, (3) 400°C, and (4) 500°C.

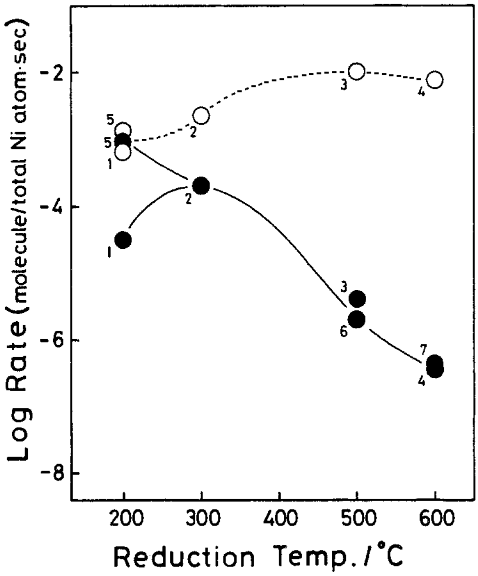

Fig. 5. Changes in the ethane hydrogenolysis activity (at 240°C) after the sequential oxidation–reduction treatments (the starting materials: (○)NiO/SiO_2, (●)$NiNb_2O_6/SiO_2$). The numbers in the figure mean the order of the H_2 treatment preceded by the O_2 treatment at 500°C.

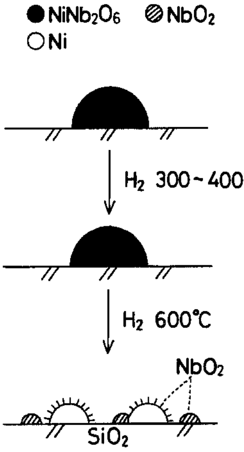

Fig. 6. A model for structural transformation of NiNb$_2$O$_6$ supported on SiO$_2$ during the H$_2$ reduction treatment.

Once the NiNb$_2$O$_6$ particles decompose, the catalyst shows the typical SMSI behavior (Nos. 5, 6, and 7): the activity is increased by O$_2$ treatment at 500°C followed by low-temperature reduction (LTR) at 200°C (No. 5), and decreased again by HTR at 600°C (No. 7). For the NiO/SiO$_2$ catalyst, the catalytic activity was not suppressed, but increased slightly with increasing H$_2$ reduction temperature probably due to the complete reduction of NiO to Ni metal (see fig. 4). The degree of the activity suppression of the NiNb$_2$O$_6$/SiO$_2$ catalyst after HTR at 600°C is more than three orders of magnitude, compared with that after LTR at 200°C. The activity change is about two orders of magnitude, even if compared between LTR at 300°C and HTR at 500°C. Ko et al. [9] studied the change of the ethane hydrogenolysis activity of niobia-modified Ni catalysts (Ni/Nb$_2$O$_5$–SiO$_2$), and observed the activity suppression by about one order of magnitude with increasing the reduction temperature from 300 to 500°C. For a niobia-supported Ni catalyst (Ni/Nb$_2$O$_5$), the activity suppression was about 1.5 orders of magnitude with increasing the reduction temperature from 300 to 500°C [8]. Therefore, the extent of the Ni–niobia interaction in the present catalyst system appears to be stronger than those of the Ni/Nb$_2$O$_5$–SiO$_2$ and Ni/Nb$_2$O$_5$ catalysts [8,9]. From the data Nos. 1 and 2, the NiNb$_2$O$_6$ particles appear to exhibit some activities for ethane hydrogenolysis since the Ni double-oxide is not reduced in H$_2$ at 300°C (see fig. 6). Similar results have been obtained for the RhNbO$_4$ catalysts [1,3]. One possible interpretation is that the surface reduction occurred even if the bulk double-oxide particles are not reduced at these temperatures.

Table 1 shows the results of cyclohexane reaction on the Ni niobate and unpromoted Ni catalysts after the O$_2$ and H$_2$ treatments. Although the bulk NiNb$_2$O$_6$ particles are not reduced by LTR at 300°C, the catalyst showed an activity with a good selectivity to benzene (85%). The turnover frequency (TOF) decreased after

Table 1
The effects of the catalyst treatments on the activity (TOF) and selectivity of cyclohexane reaction over the Ni catalysts

Catalyst [a]	Treatment [b]	Catalyst structure [c]	Particle size [c] (nm)	TOF [d]	Selectivity to benzene [e] (%)
$NiNb_2O_6/SiO_2$	LTR	$NiNb_2O_6$	8.2	9.7	85
	HTR	$Ni + NbO_2$	10.6	3.4	100
	LTR [f]	$NiO + Nb_2O_5$	7.0	21.7	46
Ni/SiO_2	HTR	Ni	11.8	11.1	22
	LTR [f]	NiO	7.0	16.5	5

[a] Calcined in air at 750°C.
[b] LTR: H_2 reduction at 300°C, HTR: H_2 reduction at 600°C.
[c] Based on the XRD measurement.
[d] Based on the particle size by XRD; $\times 10^{-3}$ s^{-1} at 300°C.
[e] The other products were due to hydrogenolysis (the main product, CH_4).
[f] After the HTR, the catalyst was treated by O_2 at 500°C followed by LTR at 300°C.

the decomposition of $NiNb_2O_6$ by HTR, while the selectivity of dehydrogenation increased to 100%. The severe suppression of the activity in the hydrogenolysis reactions, which require large ensemble sites [10,15], is characteristic of SMSI behavior [1–7]. After the O_2 treatment at 500°C followed by LTR, the TOF value of the $NiO + Nb_2O_5$ catalyst increased significantly, but the selectivity of dehydrogenation decreased. For the unpromoted Ni and NiO catalysts, the selectivity of hydrogenolysis increased significantly.

These results demonstrated that the selectivity of cyclohexane dehydrogenation is improved by the Ni–niobia interaction. However, the Rh catalysts are superior to the Ni catalysts: the dehydrogenation activity as well as the selectivity increased by the decomposition of $RhVO_4$, $CuRh_2O_4$, and $RhNbO_4$ [7,16]. It should be noted that $NiNb_2O_6$ is much more tolerant in H_2 than the Rh double-oxide such as $RhVO_4$ and $RhNbO_4$. The higher temperature (600°C) is needed for the reduction of $NiNb_2O_6$, while $RhNbO_4$ and $RhVO_4$ are reduced even by LTR at 300 and 200°C, respectively [2,4]. Because of the higher-reduction temperature, the Ni metal is not so highly dispersed by the decomposition of $NiNb_2O_6$, as shown in table 1. The preparation of such double-oxide compounds in the supercages of NaY zeolite [14] would be effective to obtain high-dispersion metal catalysts with different degrees of metal–oxide interactions.

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