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Catalytic Activity of Nb-Si Mixed Oxides Induced by Reduction with Hydrogen

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Mixed oxides of niobium and silicon became catalytically active for butene isomerization by a reduction with hydrogen, and their catalytic activities depended on the duration of the reduction. The activity was irreversibly poisoned by oxygen. The formation of Nb^{4+} by the hydrogen reduction was revealed by ESR technique. Nb^{4+} was oxidized to Nb^{5+} by the admission of oxygen gas, and at the same time O_2^- was formed. It was concluded that the catalytically active site on the mixed oxide surface was Nb^{4+} ion formed by the reduction. The importance of isolation of Nb^{4+} ion in silica network was suggested for the retention of the catalytic activity.

It has been pointed out that the geometry of a surface in the molecular dimension, such as a step or kink, is an important factor for metal crystalline catalysts resulting in structure sensitive and insensitive reactions.[1] For metal oxide catalysts, however, it is still not clear whether this type of concept can be a leading principle for interpreting their catalytic activity, since most of metal oxide catalysts are amorphous in their structure in the working state. Even for some oxides of tungsten,[2] vanadium,[3] and rhenium,[4] whose catalytic activities depend on their type of crystal phase, a relation between their catalysis and the microscopic geometry of their surface has not yet been well understood.

The authors have observed that niobium oxide, which was catalytically inactive for butene isomerization, became active for a reaction through only a slight reduction in the mixture of hydrogen gas and water vapor.[5] The catalytic activity induced by the reduction depended on the extent of the reduction; it increased with the extent of the reduction up to a composition of $NbO_{2.494}$, and then decreased by a further reduction, though the niobium oxide of the compositions between $NbO_{2.500}$ and $NbO_{2.488}$ maintains a T-type crystal structure. These facts have led us to the idea that the high dispersion of niobium(IV) ions, which is achieved by a slight reduction, is important for maintaining the catalytic activity of the reduced niobium oxide.[5] In other words, the geometric environment around Nb^{4+}, which depends on its dispersion, may determine whether Nb^{4+} becomes catalytically active or not.

To elucidate the roll of the dispersion for catalysis on reduced niobium oxide, the authors have examined the catalytic properties of mixed oxides of niobium and silicon, since niobium ions are probably dispersed in an inactive matrix of silica. The amount of Nb contained in the oxide can be changed to a wide extent so that the dispersion can be controlled over a wide range.

Experimental

Preparation of Catalysts. Niobium chloride with a purity of 99.97% (kindly supplied by Prof. Nangyo at Tohoku Univ.) was dissolved into ethanol at a concentration of 0.1 mol-Nb/l under a dry nitrogen atmospher. This solution was mixed with ethyl orthosilicate(Wako Chemical Co., Research Grade) and stirred for 0.5 h. A coprecipitate obtained by adding agueous ammonia to the above-mentioned mixture was aged for 14 h at room temperature. The coprecipitate was heated at 373 K to remove ethanol and was washed with deionized water until chloride ion was undetectable by a test with an aqueous silver nitrate solution. It was then dried on a hot-water bath and calcined at 873 K for 2 h in air. The catalyst is denoted as Nb-Si(number), where the number in the parentheses indicates 100 Nb/(Nb+Si). The X-ray diffraction spectra of the catalysts showed that they maintained an amorphous structure, even after being calcined at 873 K, though pure niobium oxide was crystallized by calcination at the same temperature, indicating that niobium atoms were well dispersed in the oxides so as to be unable to form an ordered structure.

Procedures. The reaction was carried out with a conventional gas-circulation system of 320 ml. A catalyst of 50 mg was heated at 823 K in oxygen gas for 1 h and then degassed for 0.5 h. The catalyst was reduced with hydrogen gas at 823 K. Water formed by the reduction of the catalyst was collected with a trap cooled with liquid nitrogen. After cooling the catalyst to 298 K, the reaction was started by introducing *cis*-2-butene to the reaction system. The composition of the reaction mixture was determined by gas chromatography.

ESR Measurement. The ESR spectra were recorded with a JEOL-PE-1X at 77 K. The catalyst was pretreated in the same manner as described in the above section. A tube made of quartz for ESR measurements was connected to the upper part of the reaction cell. The catalyst preliminarily pretreated in the cell was transferred to the tube for ESR measurements. A small space was provided at the top of the tube to admit oxygen gas onto the catalyst. For the observation of a tetracyanoethylene (TCNE) radical, a benzene solution of TCNE (1 ml, 8×10^{-2} mol l^{-1}) was brought into contact with the pretreated catalyst in the ESR tube. The spin density was determined by a comparison of the ESR signal of the samples with that of Mn^{2+} inserted in the ESR cavity. The latter has been frequently titrated by a standard benzene solution of DPPH in the same condition of ESR measurements applied to the samples.

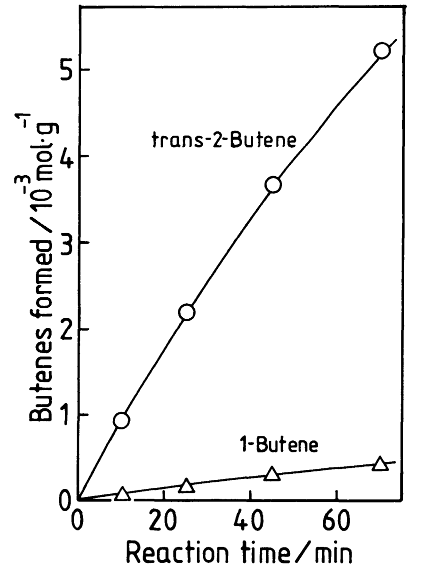

Fig. 1. Isomerization of *cis*-2-butene on the reduced Nb–Si(10). The catalyst was reduced with hydrogen gas at 823 K for 2.5 h. The reaction was carried out at 298 K with a pressure of *cis*-2-butene, 1.33×10^5 Pa.

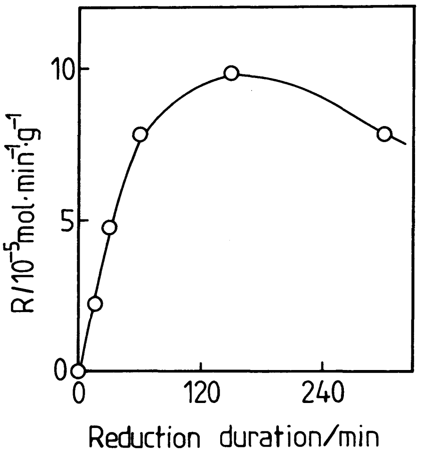

Fig. 2. Dependence of the catalytic activity of the Nb–Si(10) mixed oxide on the reduction duration at 823 K. The reaction conditions were the same as in Fig. 1.

Table 1. Poisoning of the Reduced Nb–Si(10) Mixed Oxide Catalyst

Additive	Non	O_2	NO	N_2O	CO	NH_3
Amount[a]	—	0.8	6.0	6.0	6.0	6.0
Activity[b]	2.3	0.2	0.0	1.2	1.8	0.7

a) The amount of the additives admitted/10^{-5} mol g^{-1}.
b) The catalytic activity/10^{-5} mol min^{-1} g^{-1}. The catalyst was reduced at 823 K for 0.25 h before the experiment.

Results and Discussion

Isomerization of *cis*-2-Butene. The Nb–Si mixed oxide, itself, was catalytically inactive for the isomerization of *cis*- 2-butene. It became catalytically active for the reaction by its reduction with hydrogen gas at 823 K. Figure 1 shows the progress of a reaction on Nb–Si(10) reduced for 2.5 h. Products were only 1-butene and *trans*-2-butene. The rate of the formation of *trans*-2-butene was 10-times faster than that of 1-butene. The average rate of the reaction calculated from the amount of *cis*-2-butene converted to 1-butene and *trans*-2-butene during the initial 10 min was taken as a measure of the catalytic activity.

Figure 2 shows the dependence of the catalytic activity on the reduction duration of the oxide (Nb–Si(10)). The catalytic activity could be increased by increasing the reduction duration (by up to 2.5 h) and slightly decreased upon further reduction. The induction of catalytic activity by reduction with hydrogen gas suggests that the catalytically active site for butene isomerization is a Nb cation with a lower oxidation state formed by reduction.

The catalytic activities observed for the reduced catalyst, which was preliminarily exposed to various compounds, are listed in Table 1. All the tested compounds (O_2, NO, NH_3, CO, and N_2O) retarded the catalytic activity. NO and O_2 were the most poisonous to the catalyst among them. Figure 3 shows the relation between the catalytic activity on Nb–Si poisoned by oxygen and the amount of oxygen admitted. The admission of oxygen of 5×10^{-6} mol g^{-1} reduced the catalytic activity to 1/10 of that of non-poisoned catalyst.

Oxidants, such as O_2 and NO, were the most effective poisons. However, NH_3 was less poisonous than these two compounds. Therefore, it is stressed

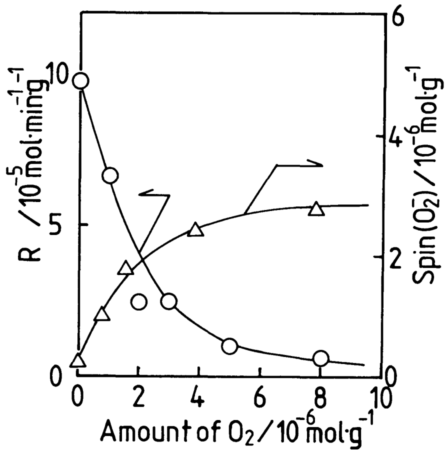

Fig. 3. Poisoning of the catalytic activity and the formation of O_2^- radical on the surface by admission of oxygen gas. The reaction conditions were the same as in Fig. 1.

that the observed activity is not attributed to the catalysis by the acidic property of the Nb-Si oxide, although Iizuka et al. have reported on the acid catalysis by hydrated niobium oxide.[6] The strong poisoning effect of the two oxidants suggests that the active site loses its catalytic activity by oxidation. Therefore, it is reasonable to assume that the active site is a Nb^{4+} ion formed by reduction with H_2. This assumption is supported by the experimental result that the formation of Nb^{4+} by reduction was assured by ESR spectroscopy for niobium oxide, which became catalytically active by reduction.[1]

ESR Investigation. While the catalysts showed no ESR absorption after a pretreatment, their reduction induced the spectrum shown in Fig. 4-a. An apparent *g* value of 1.91±0.02 was obtained, independent of the content of niobium, except for pure niobium oxide. Since the *g* value is similar to those reported for a Nb^{4+} ion in silicate glass,[7] the ESR absorption observed for the reduced Nb-Si oxide is attributed to the Nb^{4+} ion. The poor resolution of the spectrum might be due to a low symmetry and irregularity of the environment around the ions.

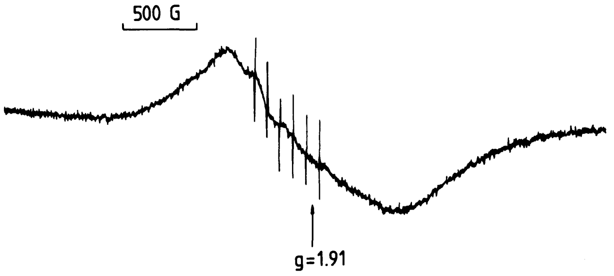

Fig. 4-a. ESR spectrum measured at 77 K of the reduced Nb-Si(50). The catalyst was reduced with hydrogen gas at 823 K for 0.25 h. The six sharp signals overlapping that of Nb^{4+} are due to Mn^{2+} as the standard.

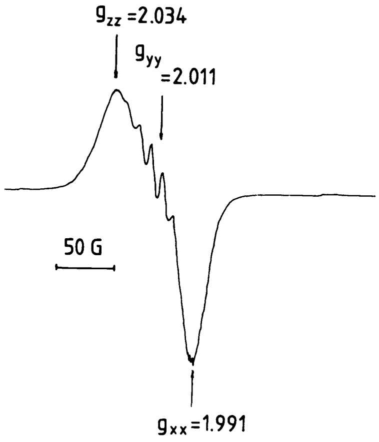

Fig. 4-b. ESR spectrum of O_2^- formed by admission of oxygen gas onto the reduced Nb-Si(10). The catalyst was reduced at 823 K for 2.5 h before the admission of oxygen gas.

When oxygen gas was admitted onto the reduced catalyst, a new signal (Fig. 4-b) appeared. The *g* values (g_{xx}=1.991±0.001, g_{yy}=2.011±0.001, and g_{zz}= 2.034±0.005) were obtained. The shape of the spectrum is similar to that of the O_2^- formed on La_2O_3 (reported by Wang et at.[8]) and on other materials.[9,10] When ethene or propene was brought into contact with a catalyst showing the ESR spectrum of Fig. 4-b at room temperature, no change in the spectrum occurred, that is, the species formed on the catalysts by the admission of oxygen gas did not react with the olefins. From the *g* values, the shape of the spectrum, and the poor reactivity with olefins, the species giving the ESR absorption spectrum of Fig. 4-b could be identified as being an O_2^- ion. Since the ESR absorption due to Nb^{4+} was decreased, in contrast with the formation of O_2^-, this O_2^- ion must be formed by electron transfer from Nb^{4+} ion as shown in Reaction 1:

$$Nb^{4+} + O_2 \rightarrow Nb^{5+} \cdots O_2^-. \qquad (1)$$

That the hyperfine structure in the spectrum resulted from an interaction of O_2^- with the niobium nucleus (I=9/2) indicates that O_2^- is located at a Nb atom. It is plausible that the hyperfine structure observed in the spectrum resulted from an interaction of O_2^- with a niobium nucleus (I=9/2), although the series of hyperfine signals can not be completely identified in the spectrum because of the low resolution of the ESR spectrum. The relation between the amount of O_2 admitted and that of O_2^- formed is shown in Fig. 3. The spin density of O_2^- formed was increased linearly up to the amount of admitted O_2 (2×10^{-6} mol g^{-1}) at a slope of unity, suggesting that O_2 was stoichiometrically converted to O_2^- on the reduced catalyst.

The inverse changes of the catalytic activity and the amount of O_2^- formed by the admission of O_2 shown in Fig. 3, strongly support the idea that the

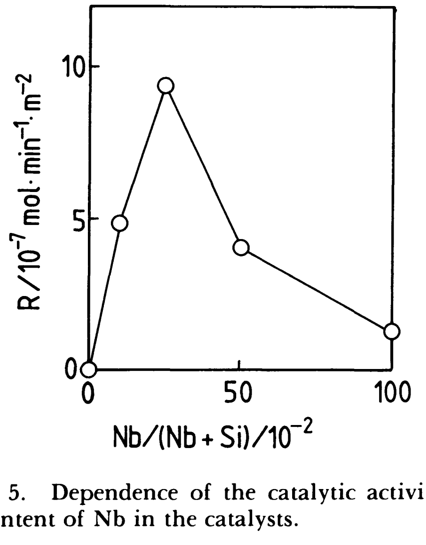

Fig. 5. Dependence of the catalytic activity on the content of Nb in the catalysts.

catalytically active site is a Nb^{4+} ion. Poisoning of the catalytic activity for butene isomerization by O_2 must be caused by the oxidation of Nb^{4+}, as indicated in Reaction 1. The number of the active sites was estimated to be 4×10^{-6} mol g^{-1} from an extrapolation of the linear part obtained at small amounts of the admitted O_2 (Fig. 3).

Catalysis and Content of Nb. Figure 5 shows the catalytic activity for *cis*-2-butene isomerization obtained on reduced Nb–Si catalysts containing various amounts of niobium. The catalytic activity showed a maximum at a content of 25%-Nb and decreased above this value. Figure 6 shows the amount of O_2^- formed on the reduced catalysts after the admission of a sufficient amount of oxygen gas to convert all Nb^{4+} to Nb^{5+} on the surface. The amount of O_2^- formed passed through a maximum at 10% of Nb and was decreased for the Nb content more than the value. Though the color change of the catalysts after a treatment with hydrogen at 823 K confirmed the occurrence of the reduction of the catalysts, almost no formation of O_2^- was observed for Nb–Si(50) and Nb–Si(100), or Nb_2O_5.

When TCNE was brought into contact with a reduced catalyst, a new ESR absorption spectrum of a single peak (g=2.011) appeared. It has been reported that TCNE is converted to its anion radical when the species with electron-donating character is present on the solid surfaces.[11,12] It is reasonable to say that a TCNE molecule, whose electron affinity is larger than that of oxygen molecule, can be converted to its anion radical on reduced Nb–Si where Nb^{4+} acts as an electron donor. Figure 7 shows the relation between the Nb content in the catalysts and the amount of TCNE radical formed on catalysts pretreated in the same manner as mentioned in Fig. 6. The TCNE radical increased linearly with an increase in the Nb content. The monotonous increase in the TCNE radical with an increase in the Nb content simply results from the increase in the amount of Nb^{4+} on the surface of the reduced catalysts. On the other hand, the O_2^- formation showed an optimum for change of the Nb atom content in the oxide. These contrasted results for the two electron acceptors, TCNE and O_2, may be explained as described below; an O_2^- radical is stable only on the isolated Nb atom on the surface, since this radical is further reduced to be an ESR inactive oxygen species, such as O_2^{2-} or O^{2-}, by a neighboring Nb^{4+}. On catalysts containing a small amount of Nb, the number of isolated Nb atoms is increased with an increase in the Nb content, since the atoms are highly dispersed. At a high content, however, the local aggregation of niobium ions occurs so as to result in a decrease in the number of isolated Nb^{4+} ions.

The resemblance in the dependences of the catalytic activity and the formation of O_2^- suggests that highly dispersed Nb^{4+} ions are catalytically more active than aggregated ions.

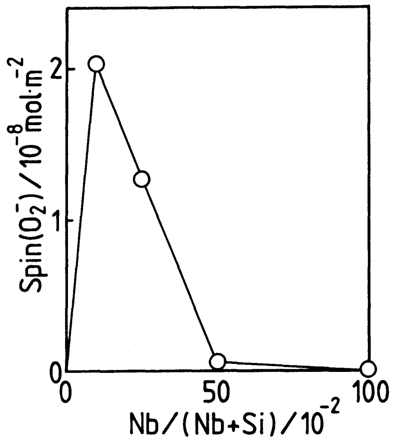

Fig. 6. Dependence of the amount of O_2^- on the content of Nb. The catalysts were reduced at 823 K for 2.5 h before the admission of oxygen gas.

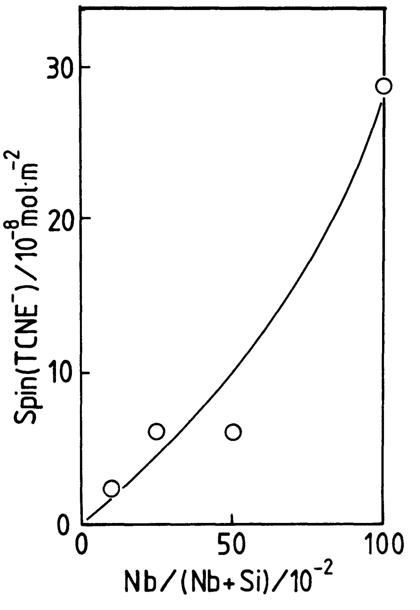

Fig. 7. Dependence of the amount of TCNE anion radical on the content of Nb in the catalysts. The catalysts were reduced at the same conditions as in Fig. 6.

The dependence of the catalytic activity observed over slightly reduced niobium oxide on the Nb/O ratio in the oxide has been explained by a change in the dispersion of Nb^{4+} formed on the surface.[5] It has been concluded that an isolated Nb^{4+} ion with coordinative unsaturation, which is formed predominantly on a highly dispersed surface, is the catalytically active site. Coordinative unsaturation is lost by coupling of two Nb^{4+} ions on a catalyst with low dispersion. It is, therefore, stressed that similarly to a reduced Nb_2O_5 catalyst[5] the catalytic activity for a Nb–Si system originates from a coordinative unsaturation of the Nb^{4+} ion.

The importance of the dispersion of active species on the surface has been reported for Nb_2O_5/SiO_2,[13] MoO_3/SiO_2,[14] MoO_3/porous Vycor glass,[15] TiO_2/porous Vycor glass,[16] Ti–Si mixed oxide,[17] and MoO_3/Al_2O_3.[18,19] Nishimura et al. have demonstrated that well-defined Nb monomers attached on SiO_2 exhibited high activity and selectivity for the dehydrogenation of ethanol.[13] Ono et al. have attributed the catalytic activity of MoO_3/SiO_2 for dehydrogenation of ethanol to tetrahedrally coordinated Mo ion formed predominantly at high dispersion.[14]

The coordination environment of metal ions in metal oxides, such as the coordination number and symmetry, which are important for the induction of catalytic activity, should depend on the dispersion for both supported oxide and mixed oxide systems. Especially for Nb–Si mixed oxide system, an isolated Nb^{4+} ion is more stable than that formed in Nb_2O_5, since a Nb atom is isolated in a matrix of silica at a low content of Nb during the preparation process.

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