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Catalytic Activity of Nonstoichiometric Niobium Oxide with Controlled Composition, $NbO_{2.488-2.500}$, for Butene Isomerization

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The composition of niobium oxide was controlled between $NbO_{2.488}$ and $NbO_{2.500}$ by treating with mixture of water vapor and hydrogen gas at 873K. X-ray diffraction (XRD) study of the treated niobium oxide showed that only a phase of nonstoichiometric T-Nb_2O_5 was found in the range of $NbO_{2.488-2.500}$ and a phase of NbO_2 coexisted with the T-Nb_2O_5 phase by further reduction. The catalytic activity of the oxide for *cis*-2-butene isomerization had a maximum value at the O/Nb ratio of 2.494. The electron spin concentration of Nb^{4+} ion, and the amount of nitrogen monoxide adsorbed on the niobium oxide also showed a maximum value at the O/Nb ratio of 2.496 and 2.494, respectively. Coincidence in the dependences, on the composition of the reduced niobium oxide, of the catalytic activity, the spin concentration of Nb^{4+} ion, and of the amount of adsorbed nitrogen monoxide shows that isolated Nb^{4+} ion with unsaturated coordination is a catalytically active site.

Niobium oxide has been often used as a promoter of catalysts, but has been recently examined as a main component of catalysts by several investigators.[1-10]

Morikawa et al. have reported that niobium oxide supported on silica became catalytically active for dimerization of ethylene both by UV light irradiation in the presence of olefin and by reduction with hydrogen at high temperature.[1] The catalytic activity of the niobium oxide catalyst activated by both the processes has been attributed to a reduced niobium species like Nb^{4+} ion. Many phases are present for reduced niobium oxide.[11] It has been reported that a specific phase of the various oxide catalysts, tungsten,[12-14] vanadium,[15] and rhenium oxides,[16] plays an important role on their obtaining catalytic activities. It is therefore supposed that the catalytic activity of niobium oxide should be closely related to the composition of niobium and oxygen atom, or the type of phase of the oxide.

We have found in this study that the composition of niobium oxide is controlled between $NbO_{2.488}$ and $NbO_{2.500}$ without change of its phase by the treatment with mixtures of water vapor and hydrogen gas in various ratios. The reaction experiment with the isomerization of butene carried out on the niobium oxide with the various controlled compositions have revealed the relationship between the structure of the oxide and its catalytic activity.

Experimental

Materials. A standard material of niobium oxide, $NbO_{2.500}$ was prepared from niobic acid manufactured by CBMM INT. LTDA. (#AD378). This niobic acid contained the impurities of Fe (40 ppm), Na (23 ppm), K (27 ppm), and Si (490 ppm). Niobic acid was dried in air at 673 K for 3 hours and calcined at 873 K for 30 hours. The X-ray diffraction (XRD) pattern of the oxide was attributed to the T-Nb_2O_5 structure.[17] Oxygen and hydrogen were purified by passing through 4A Molecular Sieve cooled to the Dry Ice temperature. Water and *cis*-2-butene were used after bulb-to-bulb distillation in vacuo.

Control of the Composition of Niobium Oxide. The treatment of niobium oxide for its control of the composition was carried out with a closed gas-circulation system. The standard oxide of 1 g was heated up to 873 K in the stream of oxygen gas. After the oxygen gas was evacuated for 30 min, the H_2O-H_2 mixture was brought into contact with the oxide. The H_2O-H_2 mixture was circulated by a magnetically driven piston pump installed in the gas-circulation loop. Excess amount of water was stored at U shape trap of the circulation system cooled at a temperature between 233 and 283 K to keep a constant partial pressure of water vapor in the H_2O-H_2 mixture. Initial pressure of hydrogen was 13.3 kPa. After the pressure drop of the gas was ceased, the sample was quenched by rapid cooling to 298 K. The composition of niobium oxide prepared by the treatment is calculated from the pressure decrease of the mixture. The composition is expressed by the atomic ratio, O/Nb, with precision of ± 0.0005. The surface area (15 $m^2 g^{-1}$) of the oxide was unchanged by the treatment.

Reaction Experiments and Spectroscopy. The reaction of *cis*-2-butene was carried out at 298 K with a closed circulation system. The reaction mixture was analyzed by gas chromatography. XRD was measured with Rikadenki Rotaflex RU-200. Electron spin resonance (ESR) spectra were recorded at 77 K by JEOL-PE-IX spectrometer. The sample was transferred to an ESR tube and sealed in vacuo.

Results

Control of O-Nb Composition. In Fig. 1, the changes in the composition of niobium oxide indicated by the ratio, O/Nb, during the treatments at 873 K with the H_2O-H_2 mixtures of various H_2O/H_2 ratios are displayed. When the standard sample was treated in the H_2O-H_2 mixture of the partial pressure ratio of $P_{H_2O}/P_{H_2}=9.0\times10^{-3}$, the ratio of oxygen and niobium atom in the oxide was decreased up to the value of O/Nb=2.498 and no further reduction was observed. This composition did not change even after 6 hours of the treatment. When the sample which was preliminarily reduced to the ratio of O/Nb=2.482 was kept into contact with the H_2O-H_2 mixture of ratio, $P_{H_2O}/P_{H_2}=9.0\times10^{-3}$, the O/Nb value was increased to 2.498, which was coincident with the value observed when the standard sample with O/Nb=2.500 was

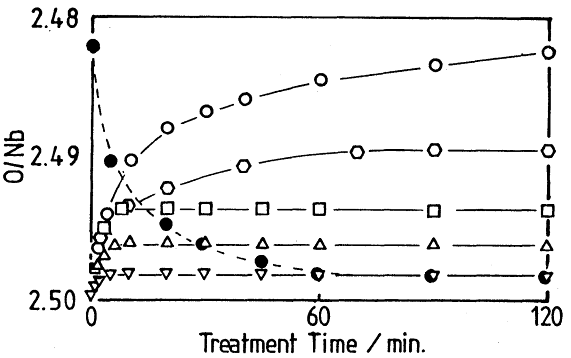

Fig. 1. Change in the O-Nb composition during the treatment with H_2O-H_2 mixture at 873 K. The ratios of the mixture, P_{H_2O}/P_{H_2}, are 2.0×10^{-3} (○), 4.0×10^{-3} (○), 8.0×10^{-3} (□), 3.0×10^{-2} (△), and 9.0×10^{-2} (▽). The broken line shows change in the composition of $NbO_{2.483}$, when it was treated with the H_2O-H_2 mixture of the P_{H_2O}/P_{H_2} ratio, 9.0×10^{-2} (●).

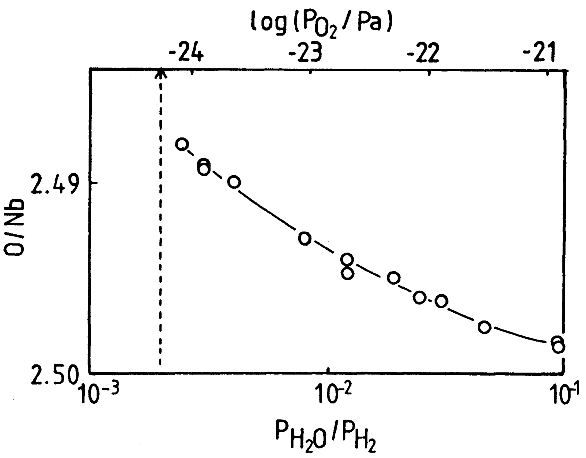

Fig. 2. Dependence of the equilibrium composition of niobium oxide on P_{H_2O}/P_{H_2} at 873 K. The partial pressure of oxygen is denoted by P_{O_2}.

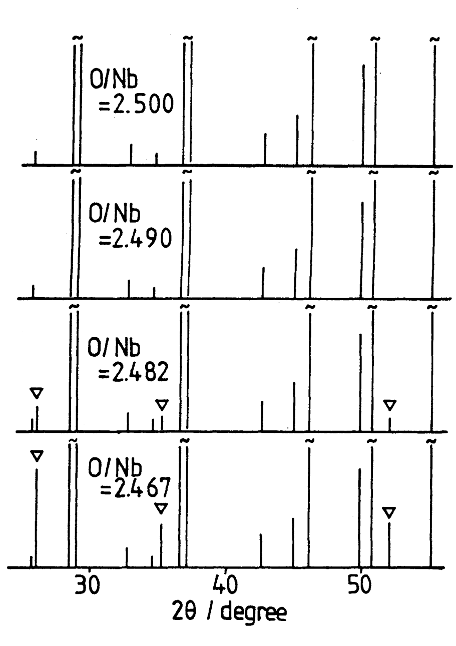

Fig. 3. XRD patterns of niobium oxide of the various composition obtained by the treatment. ($K\alpha$=0.15418 nm).

treated by the H_2O-H_2 mixture of the same ratio. It is, therefore, stressed that oxidation and reduction of the oxide are reversible and the oxide is in equilibrium with the H_2O-H_2 mixture.

The treatment with the H_2O/H_2 mixture of the ratio 3.0×10^{-2}, 8.0×10^{-3}, or 4.0×10^{-3}, gave the reduced oxides with the corresponding O/Nb ratio, 2.496, 2.493, or 2.490, respectively. When the mixture of $P_{H_2O}/P_{H_2}=2.0\times10^{-3}$ was used, the O/Nb value continuously decreased and did not show a stable equilibrium composition. It was reduced to the O/Nb ratio further less than 2.475 by the treatment of 6 hours.

The careful examination of the O/Nb values corresponding to the various P_{H_2O}/P_{H_2} values of the reducing gas mixture in the range of 1.0×10^{-1}—2.5×10^{-3} yielded the result shown in Fig. 2. The partial pressure of oxygen calculated from the equilibrium of water decomposition is expressed in the figure. The value of the O/Nb ratio decreased with decrease in the ratio of P_{H_2O}/P_{H_2} between 1.0×10^{-1} and 2.5×10^{-3}. A discontinuity in the O-Nb phase at the O/Nb ratio of 2.488 was present in Fig. 2.

XRD Measurements of Niobium Oxide. Figure 3 shows X-ray diffraction patterns of niobium oxide which was rapidly quenched by cooling after the treatment described in the above section. The standard Nb_2O_5 (non-reduced) is identified as T-Nb_2O_5 type crystal structure by XRD pattern.[17] The observed XRD patterns show that niobium oxide reduced up to the composition of O/Nb=2.490 maintains the crystal structure of T-Nb_2O_5, although the careful analysis of the patterns revealed a slight lattice expansion by the reduction in respect to all the three crystal axes. It is, therefore, suggested that only a nonstoichiometric T-Nb_2O_5 phase is present in the range of the O/Nb ratio, 2.500—2.488.

When the oxide was further reduced to $NbO_{2.482}$, new peaks marked by ▽ signs in the figure appeared at *d* values of 0.343, 0.255, and 0.176 nm, which were attributed to NbO_2.[18] The intensity of the peaks due to NbO_2 increased with decrease in the O/Nb ratio of the oxide. Therefore, it is concluded that two phases coexist below the O/Nb ratio of 2.488 and the nonstoichiometric Nb_2O_5 phase is transformed into NbO_2 phase with decrease of the O/Nb ratio.

ESR Spectrum of Nb^{4+} Ion. No ESR signal was observed for the standard oxide. The ESR absorption by the oxide was induced by its reduction. An ESR spectrum of the niobium oxide reduced to the O/Nb ratio of 2.496 by the treatment was observed as shown in Fig. 4. Its *g* value was 1.85±0.03. The spectrum was attributed to Nb^{4+} ion as discussed in the following section.

The intensity of the ESR signal changed as shown in Fig. 5 when the O/Nb composition of niobium

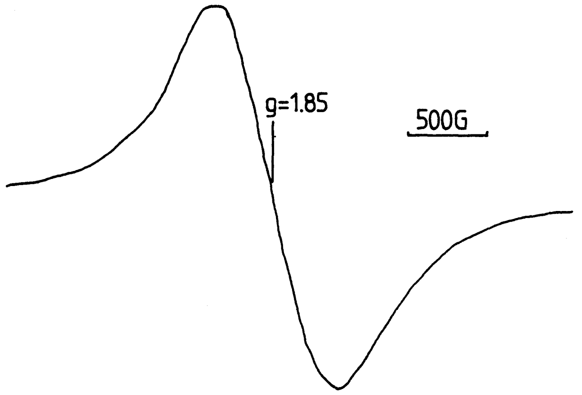

Fig. 4. ESR spectrum of niobium oxide (O/Nb=2.496) measured at 77 K after the treatment with the H_2O-H_2 mixture.

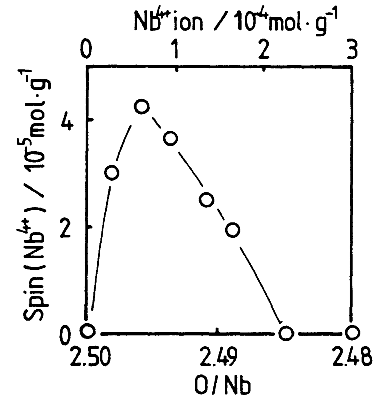

Fig. 5. Dependence of the spin concentration of Nb^{4+} ion upon the composition of niobium oxide. The spectrum was measured at 77 K. The concentration of Nb^{4+} ion estimated from the O/Nb ratio is shown.

oxide was varied. The g value was independent of the composition. The spin concentration of Nb^{4+} ion increased with decrease of the O/Nb ratio and reached a maximum value at O/Nb=2.496. The spin concentration of Nb^{4+} determined by ESR was coincided well with the amount of Nb^{4+} ions estimated from the composition of the oxide only at the low extent of reduction. Further decrease of the O/Nb ratio depressed the spin concentration and, finally, no ESR signal was observed at the O/Nb ratio below 2.485.

Adsorption of NO. The asymmetric broad signal was observed by ESR spectroscopy after the adsorption of nitrogen monoxide on the niobium oxide of the O/Nb ratio between 2.489 and 2.498 as shown in Fig. 6. The perpendicular and parallel g values of the signal are 1.996 ±0.001 and 1.93±0.01, respectively.

Figure 7 shows the change of the spin concentration of nitrogen monoxide adsorbed on the niobium oxides of the various O/Nb compositions. The spin concentration showed a maximum at the O/Nb value of 2.494, while it is lowered for the O/Nb values both lower and higher than this value.

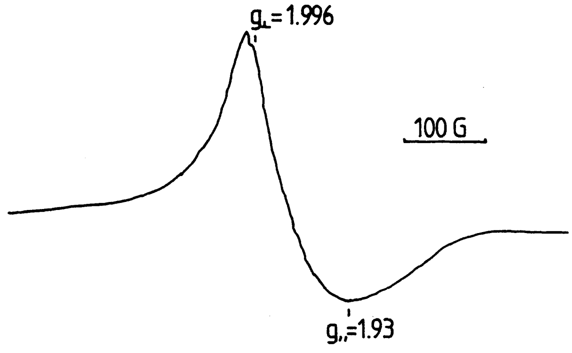

Fig. 6. ESR spectrum of nitrogen monoxide adsorbed on the treated niobium oxide (O/Nb=2.494) measured at 77 K.

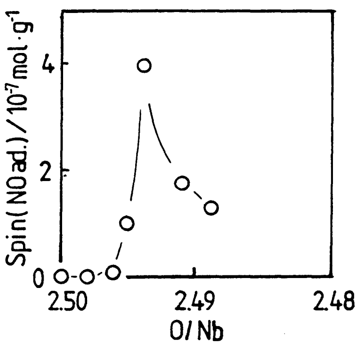

Fig. 7. Dependence of the spin concentration of nitrogen monoxide adsorbed on niobium oxide upon the composition of niobium oxide. The spectrum was measured at 77 K.

Isomerization of *cis*-2-Butene. The standard sample of niobium oxide was catalytically inactive for isomerization of *cis*-2-butene. Reduction of the oxide by the treatment with the H_2O-H_2 mixture induced its catalytic activity. Change in the amounts of isomers, *trans*-2-butene and 1-butene observed at 298K on the niobium oxide with the O/Nb ratio of 2.494, is displayed in Fig. 8. No other product was found. A short induction period was observed at the initial stage of the reaction, and the isomerization proceeded linearly to the reaction time. The slope of the linear part was taken as the rate of the isomerization of *cis*-2-butene to each isomer. The ratio of the amount of *trans*-2-butene to that of 1-butene produced was constant at the value of 10 during the reaction. The catalytic activity is represented by the rate of *trans*-2-butene formation observed at a constant pressure of the reactant, *cis*-2-butene, in this paper.

As shown in Fig. 9, the catalytic activity depended upon the O/Nb composition of niobium oxide. The catalytic activity increased with increase in the extent of the reduction, and reached a maximum value at O/Nb=2.494 and decreased with further decrease in the O/Nb value. The oxide with the O/Nb value less than 2.488 showed a very little, constant catalytic activity.

The catalytic activity observed on the oxide of the O/Nb ratio, 2.494, was poisoned completely by nitro-

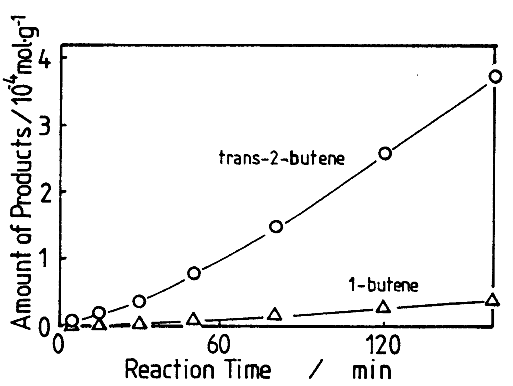

Fig. 8. Isomerization of *cis*-2-butene on the treated niobium oxide (O/Nb=2.494) along the reaction time at 298 K. Initial pressure of *cis*-2-butene was 13.3 kPa.

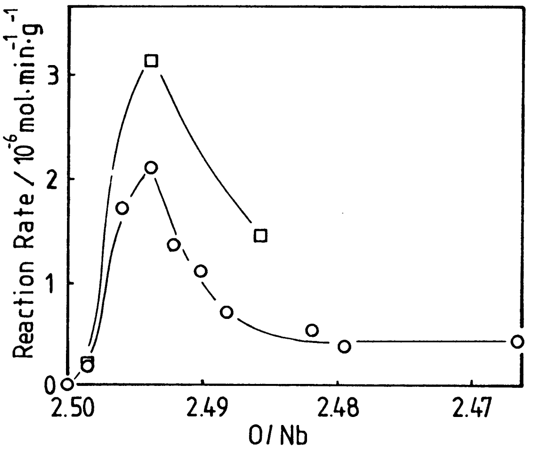

Fig. 9. Dependence of the reaction rate upon the composition of niobium oxide. The H_2O-H_2 mixture was evacuated at 298 K (○) or at 373 K (□) after the treatment.

gen monoxide of the amount, 5×10^{-6} mol, admitted both before and during the reaction.

Discussion

Crystal Structure of Niobium Oxide. It has been demonstrated that the composition of niobium oxide is controlled by the treatment with the H_2O-H_2 mixture at 873 K between the O/Nb ratio, 2.500 and 2.488. The oxide reaches in equilibrium with the H_2O-H_2 mixture in this range as described in the above section. XRD studies (Fig. 3) have clarified that the oxide maintains the T-Nb_2O_5 phase in the region between 2.500 and 2.488 of the O/Nb ratio. The continuous change of the O/Nb value against the ratio, P_{H_2O}/P_{H_2} (Fig. 2), with the slight expansion of the crystal lattice shows that T-Nb_2O_5 phase is nonstoichiometric. Continuous increase in the lattice parameters with increase in the extent of reduction observed by XRD ensures that the whole bulk of niobium oxide particles is homogeneously reduced by the treatment.

Phase relations, defect structures, and thermodynamic properties of the oxygen-niobium system above 1273 K have been reported by many investigators and have been intensively reviewed by Naito and Matsui.[11] Several oxide phases, $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{47}O_{116}$, $Nb_{25}O_{62}$, and $Nb_{53}O_{132}$ have been recognized between NbO_2 and Nb_2O_5 at 1573—1673 K by Schäfer et al.[19] and Kimura.[20] At lower temperatures 1273—1373 K, Marucco has found only two phases $Nb_{12}O_{29}$ and $Nb_{25}O_{62}$ within the same composition range.[21] In the present work, however, niobium oxide with T-Nb_2O_5 phase structure directly transforms into NbO_2 at the O/Nb ratios less than 2.488 and no suboxide phase between NbO_2 and $NbO_{2.5}$ has been found. This absence of suboxide phases is explained by the discussion of Naito et al., who have reported that the several suboxide phases with the composition between NbO_2 and $NbO_{2.5}$ were less stable at temperature lower than 1273 K.[22]

The ESR absorption observed for niobium oxide of the O/Nb ratio, 2.496, obtained by the treatment with H_2O-H_2 mixture (Fig. 4) is attributed to reduced niobium ions. The ESR absorption due to Nb^{4+} ion in pure niobium oxide was observed for the first time owing to the controlled slight reduction by the treatment with the H_2O-H_2 mixture instead of that with hydrogen gas. An ESR study of Nb^{4+} ions in silicate glasses ($n$$Na_2O$·$(98-n)SiO_2$·$2Nb_2O_5$ n=11 and 22) has been reported by Yafaev and Garif'yanov.[23] The g value in our spectrum, 1.85±0.03, was close to their g values, 1.89 and 1.92. Their ESR spectrum of Nb^{4+} ions has hyperfine structure due to the interaction of a single 4d electron with the nucleus (I=9/2) of the natural niobium isotope ^{93}Nb. The parallel and perpendicular hyperfine constants were 310 and 145 Oe in Yafaev's results. In our experiment the hyperfine structure was not observed because the spectrum was extremely broad, in which the width of magnetic field of the absorption band was about 3000 Oe as shown in Fig. 4. The spectrum of Nb^{4+} ions in our system must have been broadened by various crystallographic environment of Nb^{4+} ions in the oxide so that the hyperfine structure has been indistinguishable.

As shown in Fig. 5, when the niobium oxide is reduced further from the value of the O/Nb ratio of 2.496, the spin concentration of Nb^{4+} ion measured by ESR is decreased in spite of increase in the extent of reduction. This inconsistency is attributed to a magnetic coupling between Nb^{4+} ions. Though Nb^{4+} ion is paramagnetic and hence its signal should be observed by ESR, no ESR signal of Nb^{4+} ion was observed for NbO_2. The crystal structure of NbO_2 is described as the distorted rutile structure, resulting Nb-Nb bonding.[24,25] Thus the pairs of Nb^{4+} ions bring about spin coupling resulting in a diamagnetic character of NbO_2. In the case of molybdenum oxide the concentration of Mo^{5+} ions determined by ESR spectroscopy is lower than that evaluated from the measurement of the composition,[26] and that determined by X-ray photoelectron spectroscopy.[27,28] Abdo et al. have suggested that the Mo^{5+} ions undetectable by ESR must be strongly, magnetically coupled.[29] Our result shows that Nb^{4+} ions are detectable by ESR in nonstoichiometric Nb_2O_5 phase, because they are isolated each other in the Nb_2O_5 matrix.

A simple interpretation is given for the result shown in Fig. 5. As far as the amount of Nb^{4+} ions is very small, isolated Nb^{4+} ion is increased in T-Nb_2O_5 structure when the oxide is progressively reduced. However, when the concentration of Nb^{4+} ions exceeds a certain value, Nb^{4+} ions couple each other, causing their magnetic character to be ESR-inactive. Thus, the spin concentration determined by ESR is less than that estimated from the O/Nb ratio at a large extent of reduction. No ESR signal is observed when most of Nb^{4+} ions couple at the ratio of O/Nb greater than 2.485.

Adsorption Site of NO. ESR spectrum of nitrogen monoxide adsorbed on the niobium oxide reduced by the H_2O-H_2 mixture was observed as shown in Fig. 6. Its shape is similar to that of nitrogen monoxide adsorbed on alumina reported by Lunsford.[30] Nitrogen monoxide adsorbed on niobium oxide should provide 30 hyperfine lines due to the interaction with the nucleus of ^{14}N (I=1) and ^{93}Nb (I=9/2), but this type of hyperfine structure was ambiguous in the present experiment.

According to Lunsford's work nitrogen monoxide is adsorbed on aluminum ion which is exposed to the surface with an oxygen ion vacancy. It is plausible that the adsorption of nitrogen monoxide occurs on the oxygen ion vacancy of reduced niobium oxide. Therefore, the change of the spin concentration of nitrogen monoxide adsorbed on the reduced niobium oxide depending on the O/Nb ratio reflects the change in the amount of Nb^{4+} ion which is exposed to the surface with an oxygen ion vacancy. The similar changes of the spin concentration of Nb^{4+} and of adsorbed nitrogen monoxide along with decrease in the O/Nb ratio lead us to a new assumption that isolated Nb^{4+} ion must provide an oxygen ion vacancy, in other words, isolated Nb^{4+} ions are coordinatively unsaturated. When the isolated Nb^{4+} ions are paired, they lose coordinatively unsaturation.

Active Sites for Isomerization. Isomerization of 1-butene on niobium oxide catalyst prepared by degassing of $Nb_2O_5 \cdot nH_2O$ has been studied by Iizuka et al.[2] $Nb_2O_5 \cdot nH_2O$ degassed at 373K exhibits a substantial catalytic activity for the isomerization, attributed to a very strong Brønsted acid. Degassing of $Nb_2O_5 \cdot nH_2O$ at temperatures higher than 773 K results in a remarkable decrease in the acidity and, therefore, niobium oxide prepared by calcination at 873 K exhibits little activity for the isomerization. Therefore, it is stressed that the catalytic activity for butene isomerization on the reduced niobium oxide observed in the present work originates hardly from its acid catalysis. Actually, the addition of ammonia of which amount was in excess of that of all the reduced species on the surface did not result in the complete loss of the activity, but reduced the activity to only one-half of its original value.

No catalytic activity was observed for the non-reduced niobium oxide, while the activity for the catalytic isomerization of butene was resulted from reduction of niobium oxides, indicating that the catalytically active site of the reduced niobium oxide catalyst is attributed to the reduced species of niobium ion. Thermodynamic data tell us that Nb^{5+} ion is reduced only to Nb^{4+} but not to a lower valence niobium ions in our experimental conditions. Formation of Nb^{4+} by the treatment with the H_2O-H_2 mixture was assured by ESR spectroscopy.

As discussed above, the observed spin concentration of Nb^{4+} reflects the amount of isolated and coordinatively unsaturated Nb^{4+}. Since nitrogen monoxide strongly poisons the catalytic activity, it was adsorbed on the catalytically active site of butene isomerization. It is concluded that the catalytically active site is identical with the nitrogen monoxide adsorption site, that is, isolated Nb^{4+} ion with coordinative unsaturation. This conclusion is supported by the general agreement between the catalytic activity and the amount of the adsorbed nitrogen monoxide (Figs. 7 and 9). The reason for the difference between these two measurements on the slightly reduced catalyst is ambiguous at present.

Among the tungsten oxide catalysts, WO_{3-x}, nonstoichiometric phase shows the high activity and selectivity for the reactions, for example, oxidation of propylene,[12] and allyl iodide,[13] and decomposition of N_2O.[14] On the other hand, stoichiometric oxides, WO_3, WO_2 or a tunnel structure oxide of $WO_{2.72}$, are less active or inactive for those reactions. Metathesis of propylene on ReO_3 catalyst is enhanced by a slight reduction of the catalyst with CO, but its catalytic activity is lowered when the extent of reduction exceeds a critical value.[16] Importance of nonstoichiometric phase for the catalysis demonstrated in these systems may be explained by the same idea that isolation of catalytically active species to keep the state of coordinative unsaturation is essential to maintain high catalytic activities as demonstrated in the present system.

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