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New Reversible Enhancement/Depression Phenomenon on Catalysis of Platinum Supported on One-Atomic Layer Niobium Oxide for Ethene Hydrogenation

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While platinum supported on one-atomic layer Niobium oxide which was chemically attached on a silica surface did not exhibit an SMSI phenomenon unlike usual Nb_2O_5-supported Pt, the ethene hydrogenation activity of the catalyst reduced at 773 K was much higher than a SiO_2-supported Pt catalyst. Another interesting feature is that the activity was reversibly enhanced or depressed as a function of pre-evacuation temperature.

We have prepared the SiO_2-attached one-atomic layer Nb oxide catalyst, active and selective for intramolecular dehydration of ethanol, by using the reaction between surface silanol groups and $Nb(OC_2H_5)_5$.1) In the present article we report a new feature observed on catalysis of platinum deposited on the one-atomic layer Nb oxide, where an evidence for the one-atomic layer growth of Nb oxide on SiO_2 is also given by EXAFS analysis.

The preparation of the one-atomic layer Nb oxide on SiO_2 required the repeated(twice) interaction between surface silanols and $Nb(OC_2H_5)_5$ because the molecular size of $Nb(OC_2H_5)_5$ is nearly twice as large as that of the $NbO_{2.5}$ unit.1) This amount of Nb deposited was defined as monolayer(1 ML) which is also equivalent to the amount expected from the surface area of SiO_2 (taking into account the distribution of pore-diameters) and size of the Nb_2O_5 unit-cell. In order to examine the deposition mode(one-atomic layer or three-dimensional island growth) of Nb oxide on SiO_2, the amount of Nb oxide deposited was varied from 0.08 ML to 2 ML and those samples were characterized by EXAFS. The 2 ML sample was prepared by an impregnation method using a hexane solution of the necessary amount of $Nb(OC_2H_5)_5$.

Figure 1 shows the best-fitting results of the EXAFS oscillations Fourier-filtered in the range of 0.1-0.4 nm in the Fourier transformations of the Nb K-edge EXAFS data for 0.08 ML, 0.3 ML, 0.6 ML, 1.0 ML, and 2.0 ML Nb oxide samples. The Fourier-filtered data(solid lines) for 0.08-1.0 ML samples exhibit the shoulder structure at the $k \approx 50\ nm^{-1}$, whereas that of 2.0 ML does not. The X-ray diffraction pattern due to crystalline Nb_2O_5 was observed only with 2.0 ML sample. Nb_2O_5 powder showed no shoulder at $k \approx 50\ nm^{-1}$, either. Therefore this shoulder structure may be attributed to the Nb-Si interaction to form the one-atomic layer structure of Nb oxide. To confirm this point we carried out the curve-fitting analysis using the EXAFS theoretical equation.5) The phase shifts and amplitude functions were derived from the model compounds such as $LaNbO_4$, Nb_2O_5, and $NbSi_2$ for Nb-O, Nb-Nb, and Nb-Si bondings, respectively. The shoulder structures observed with 0.08 ML, 0.3 ML, 0.6 ML, and 1.0 ML samples were well reproduced in the calculated EXAFS oscillations (broken lines of Fig.1) only when the presence of Nb-Si bonding was assumed. The analysis results are given in Table 1. Figure 1 and Table 1 show a similarity in local Nb-structure of the samples with Nb loadings below 1 ML, besides the presence of Nb-Si bond. Thus, the EXAFS data provide an evidence for the formation of one-atomic Nb-oxide layer structure on SiO_2. This layer structure was stable at 773 K under vacuum or in H_2 because no change was observed in the EXAFS spectrum.

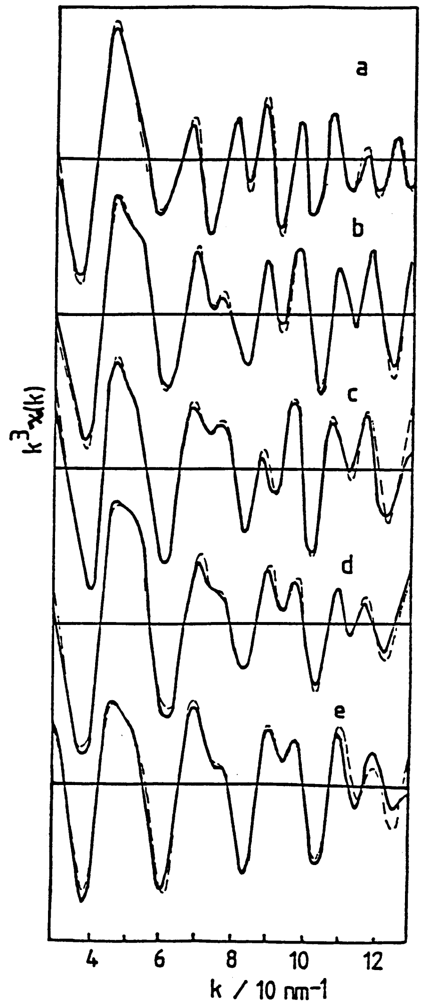

Fig.1. The Fourier-filtered EXAFS oscillations (solid lines) and the best curve-fitting results (broken lines) of SiO_2-attached Nb oxide (a): 2 ML, (b): 1 ML, (c): 0.6 ML, (d): 0.3 ML, (e): 0.08 ML.

The SiO_2-attached one-monolayer Nb oxide was impregnated with an aqueous H_2PtCl_6 solution, followed by drying at 383 K and calcination at 773 K for 2 h. The Pt catalyst thus obtained is denoted as Pt/Nb/SiO_2 hereinafter. The catalyst (Pt loading: 1 wt%) was treated at 673 K with O_2 for 1 h, and reduced with H_2 at 473 K for 1 h, followed by evacuation at various temperatures for 30 min before ethene hydrogenation at 220 K. The Nb K-edge XANES and EXAFS spectra of Pt/Nb/SiO_2 showed that the Nb oxide was not reduced with H_2 at 773 K even in the existence of the Pt particles. Again, this showed the stability of the one-atomic layer structure of Nb oxide resulting from the Nb-O-Si direct bonding. The TEM studies showed that the average sizes of Pt particles were 3.1 and 4.0 nm for Pt/Nb/SiO_2 samples reduced at 473 K and 773 K, respectively. The Pt dispersions (H/Pt) were 0.29 and 0.25 for Pt/Nb/SiO_2 reduced at 473 K and 773 K, respectively, indicating the particle sizes of 3.9 nm and 4.5 nm, respectively, when spherical shapes were assumed. It is to be noticed that the Pt particles deposited on the one-atomic layer niobium oxide showed no SMSI phenomenon in contrast to usual Nb_2O_5-supported Pt2,3) and a thin-layer Nb oxide-supported Ni.4) This non-SMSI behavior may be due to hard

Table 1. Curve-Fitting results[a)]

Sample	Nb-O			Nb-O			Nb-Nb			Nb-Nb			Nb-Si		
	N	r/nm	σ/nm	N	r/nm	σ/nm	N	r/nm	σ/nm	N	r/nm	σ/nm	N	r/nm	σ/nm
2 ML	3.8	0.207	0.095				0.7	0.315	0.078	3.9	0.389	0.066			
	(4)	(3)	(20)				(3)	(4)	(20)	(3)	(4)	(20)			
1 ML	1.7	0.194	0.070	1.0	0.211	0.070	1.2	0.342	0.065	0.7	0.378	0.060	0.8	0.327	0.070
	(3)	(3)	(20)	(3)	(3)	(20)	(3)	(4)	(20)	(4)	(4)	(20)	(4)	(4)	(20)
0.5 ML	1.6	0.195	0.060	0.8	0.213	0.080	0.8	0.343	0.060	0.7	0.379	0.065	0.7	0.325	0.070
	(3)	(3)	(20)	(3)	(3)	(20)	(3)	(4)	(20)	(4)	(4)	(20)	(4)	(4)	(20)
0.2 ML	1.7	0.192	0.070	0.8	0.209	0.060	0.8	0.339	0.060	0.8	0.376	0.070	0.5	0.330	0.050
	(3)	(3)	(20)	(3)	(3)	(20)	(3)	(4)	(20)	(4)	(4)	(20)	(4)	(4)	(20)
0.08ML	1.5	0.193	0.060	1.2	0.209	0.060	0.7	0.342	0.060	0.4	0.380	0.070	0.8	0.326	0.070
	(3)	(3)	(20)	(3)	(3)	(20)	(3)	(4)	(20)	(4)	(4)	(20)	(4)	(4)	(20)

a) N: Coordination number, r: bond length, σ: Debye-Waller factor. Parentheses show the errors.

reducibility of the one-atomic layer Nb oxide having the strong Nb-O-Si bonds as mentioned above.

Table 2 shows the catalytic activities for ethene hydrogenation at 220 K over three different types of Pt catalysts. Usual Pt/Nb_2O_5 loses its ethene hydrogenation activity by reduction with H_2 at 773 K(1.4×10^{-4} mol·(min Pt-g)$^{-1}$) compared to that of the 473 K-reduced sample(3.6×10^{-3} mol·(min Pt-g)$^{-1}$) owing to an SMSI effect. On the other hand, ethene hydrogenation on Pt/Nb/SiO_2 reduced at 773 K proceeded more rapidly by a factor of 50 than that on the sample reduced at 473 K as shown in Table 2.

Figure 2 shows the initial rates for ethene hydrogenation on Pt/Nb/SiO_2 as a function of pre-evacuation temperature. When the sample was reduced at 473 K and evacuated at 773 K, the activity was similar to that of the sample reduced and evacuated at 773 K as shown in Fig.2. In contrast, if the sample was reduced at 773 K and evacuated at 473 K, its activity became as low as that reduced and evacuated at 473 K. Thus the catalytic activity only depends on evacuation temperature rather than reduction temperature. Moreover, the steep change in activity around 673 K was observed similarly to a quasi-phase-transition phenomenon as shown in Fig.2. This

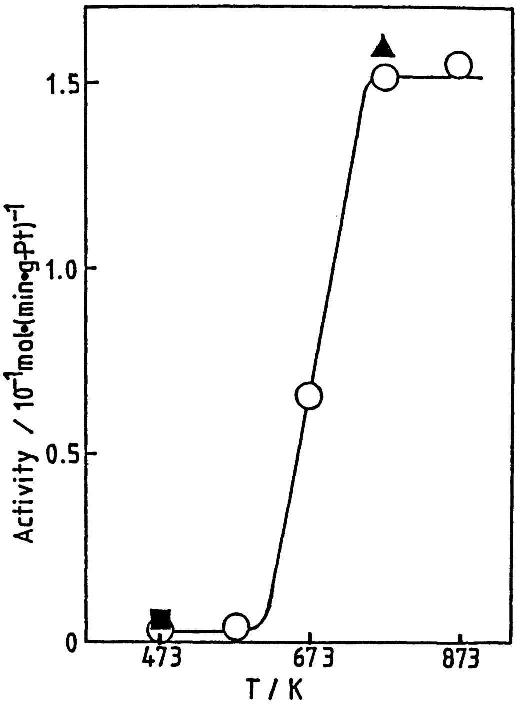

Fig.2. The dependency of activity (initial rate) of Pt/Nb/SiO_2 for ethene hydrogenation at 220 K on evacuation temperature. The sample was reduced at 473 K for 1 h and evacuated at the temperatures shown in the figure. The filled triangle and square mean the sample reduced at 773 K for 1 h and evacuated at 773 K or 473 K, respectively.

Table 2. Catalytic activity for ethene hydrogenation

Catalysts	Reduction temperature K	Activity mol·(min·Pt-g)$^{-1}$
$Pt/Nb/SiO_2$	473	3.5×10^{-3}
	773	1.6×10^{-1}
Pt/Nb_2O_5	473	3.6×10^{-3}
	773	1.4×10^{-4}
Pt/SiO_2	473	3.5×10^{-3}
	773	4.2×10^{-3}

phenomenon was reversible against the temperature in the sense that the activity was recovered without the particular oxidation or reduction treatments.

The mechanism of the reversible ca.50 times-change of the activity by the evacuation temperature is not clear at present. Sintering is not the origin of the phenomenon because little change of the dispersion was observed after the high temperature reduction. The H_2 chemisorption results may also exclude the possibility of the deactivation by impurities diffused from the bulk. Although ethene hydrogenation has long been believed as a structure-insensitive reaction,[6)] there is some evidence for the structure-sensitiveness.[7)] Recently, Uhm and Lee[8)] suggested that Pt surface treated at high temperature followed by rapid cooling could create hydrogen-strongly bound sites which may be referred to steps, kinks, and adatoms. The reversible activity change observed with our catalyst might be related to a micro-morphological change of Pt surface sites. Such active sites are preferably produced by the high temperature treatment and stabilized by the interaction with the one-atomic layer Nb oxide when cooled down to room temperature. However, the activity was depressed by the 30 min annealing at 473 K. The activity of $Pt/Nb/SiO_2$ reduced at 773 K was much higher as compared with that of Pt/SiO_2 reduced at 773 K as shown in Table 2, indicating the promotion effect of the one-atomic layer Nb oxide by this treatment.

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