

THE SURFACE STRUCTURE AND CATALYTIC PROPERTIES
OF ONE-ATOMIC LAYER AMORPHOUS NIOBIUM-OXIDE ATTACHED ON SiO₂

Kiyotaka ASAKURA and Yasuhiro IWASAWA*

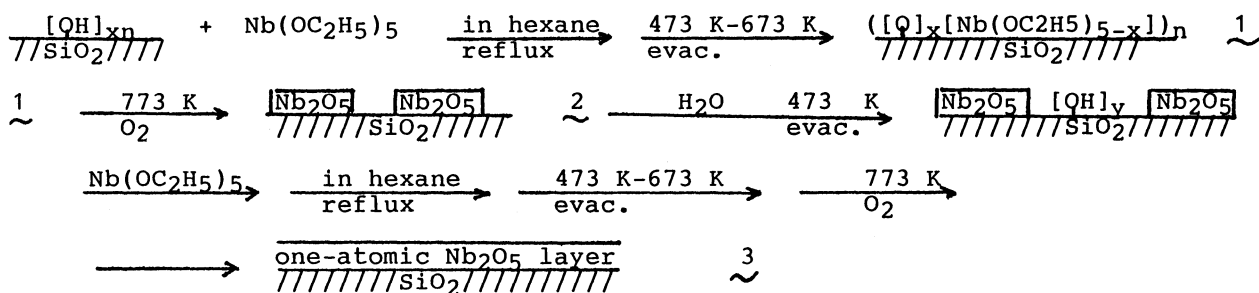
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

A SiO₂-attached one-atomic layer amorphous niobium-oxide catalyst was prepared by the two-stage attaching reaction between silanol groups and Nb(OC₂H₅)₅ followed by chemical treatments with H₂O and O₂. The one-atomic layer Nb oxide catalyst was found to be active and selective for ethene formation from ethanol.

The catalytic behaviors of transition metal oxides depend on the surface structures, environments and regularity, and electronic states of metal ions. Ultra-thin (one ~ several-atomic layers) metal-oxides spread on support surfaces are expected to have unique surface structures and electronic states which may result in noble catalytic properties. In the present work¹⁾ the preparation, structure and unique catalysis of one-atomic layer of niobium oxide spread on a SiO₂ surface were studied.

The one-atomic layer niobium-oxide catalyst was prepared as illustrated in Scheme 1. A 473 K-pretreated SiO₂ (510 m²g⁻¹, 5 OH nm⁻²) was impregnated with a dried hexane solution of Nb(OC₂H₅)₅. The amount of Nb(OC₂H₅)₅ in the solution was equivalent to the quantity of the surface OH groups. The reaction between Nb(OC₂H₅)₅ and the OH groups was conducted for 2 h under reflux conditions in Ar(99.9995%) atmosphere. After decantation of the residual solution, the sample was washed with hexane in a flow of Ar to remove the Nb(OC₂H₅)₅ remaining on the SiO₂ surface without chemical bonding and then evacuated at 473 K, followed by heating up to 673 K to complete the attaching reaction. The sample (1) thus obtained was exposed to H₂O vapor and oxidized at 773 K in air to form a half-atomic layer species (2) in Scheme 1.

Each [Nb(OC₂H₅)_{5-x}] species 1 occupies roughly 0.40 nm² at the surface, while the attached [NbO_{2.5}] unit of 2 is estimated to have a molecular area of 0.16 nm² from Nb₂O₅ structure in which the Nb-O-Nb distances are in the range of 0.28-0.4 nm.²⁾ In order to cover the SiO₂ surface completely with niobium-oxide layer, therefore the above attaching-procedure was conducted again. Thus, SiO₂-attached one-atomic layer niobium-oxide catalyst (3) was prepared. For comparison, a conventional Nb oxide catalyst with the same Nb content as that of 3 was prepared by impregnating SiO₂ with a methanol solution of NbCl₅, followed



Scheme 1. The preparation of the SiO₂-attached one-atomic layer niobium oxide.

by calcination at 773 K.

The amount of the niobium contained in the catalyst 3 (23.7 wt% as Nb / SiO₂) which was determined by means of X-ray fluorescence and gravimetry (from the Nb content in the initial and the residual solutions of Nb(OC₂H₅)₅ in the attaching reaction), was close to the amount of niobium oxide to cover the SiO₂ surface in nearly one-atomic layer. The catalyst 3 showed neither X-ray diffraction nor electron diffraction patterns of Nb₂O₅ crystal. The high-resolution transmission electron microscope gave no image of niobium oxide particles on SiO₂. The X-ray microanalysis (XMA) (scanning-intensity ratios (Nb/Si) on a SiO₂ micro-particle) of 3 suggested a homogeneous distribution of Nb atoms on SiO₂ surfaces within its resolution. On the other hand the profile of the impregnated Nb/SiO₂ catalyst showed a heterogeneous Nb-distribution, indicating the presence of island (or particle)-like Nb-oxides on the SiO₂ surface. All these results indicate that Nb atoms were attached in an amorphous-like one-atomic layer on SiO₂. The formation of OH groups on a 773 K-treated Nb₂O₅ by exposing to H₂O vapor was negligible,³⁾ while silanols (3740 cm⁻¹) were readily formed as proved by IR spectra. This fact also suggests the one-atomic layer formation by a preferential reaction of Nb(OC₂H₅)₅ with the OH groups of the exposed SiO₂ sites in the 2nd attachment step, 2 to 3 in Scheme 1. Independently of us, recently Ko et al.⁴⁾ claimed the formation of a similar amorphous one-atomic layer of Nb oxides on SiO₂ by a simpler method including one-stage deposition of Nb(OC₂H₅)₅ in hexane. However, our experience indicates that their method is liable to give the samples which involve a crystalline Nb₂O₅ phase.

To clarify the local structure around a Nb atom in the catalyst 3, X-ray absorption spectra of Nb K-edge were measured by use of synchrotron radiation.⁵⁾ The X-ray absorption near-edge structure together with the XPS binding energies of Nb 3d levels revealed that Nb exists genuinely in a pentavalent state. Figure 1 shows the EXAFS Fourier transforms with the phase shift uncorrected. The second strong peak of the Fourier transform for crystalline T-type Nb₂O₅ is straight-

forwardly assigned to Nb-Nb bond²⁾ and the bond distance was determined to be 0.376 nm by the curve fitting analysis. The main Nb-Nb bond in the catalyst 3 was observed at 0.331 nm (phase shift corrected); the value corresponds to the Nb-Nb distance for the edge-shared structures of $[\text{NbO}_6]$ units. This implies that the relative portion of the edge-shared to the corner-shared structures in the one-atomic layer catalyst 3 is much larger compared with that of T-Nb₂O₅ bulk. From the analysis of the first peaks of the Fourier transforms, the

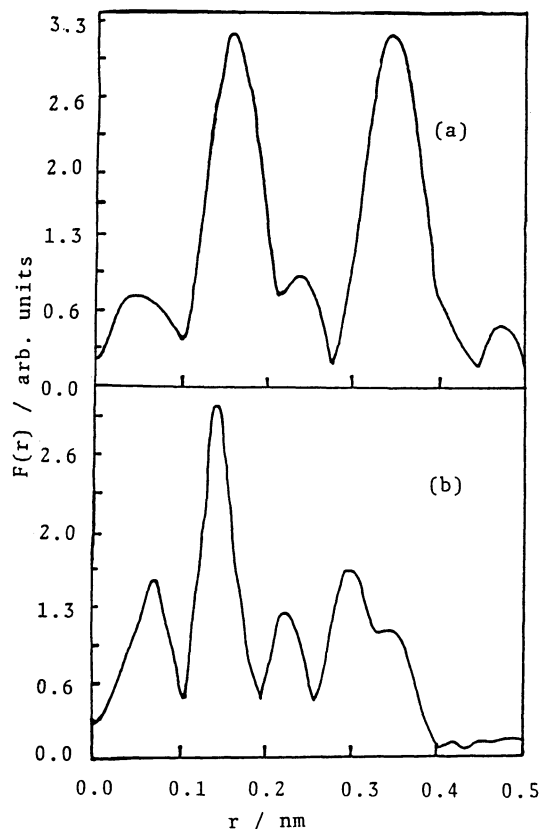


Fig. 1. Fourier transforms of k^3 -weighted EXAFS data. (a) T-Nb₂O₅ and (b) one-atomic layer niobium-oxide catalyst 3.

Nb-O bonds were determined to be 0.195 nm and 0.213 nm for the catalyst 3 and T-Nb₂O₅, respectively. The Nb-O bond length of the catalyst 3 was also different from that of Nb₂O₅. The relative intensity of Nb-Nb peak to Nb-O peak was smaller with the catalyst as shown in Fig. 1, reflecting the two dimensional amorphous phase.⁵ In addition to the Nb-O and Nb-Nb bonds, the detailed analysis for the catalyst 3 showed the presence of the Nb-Si bond, which indicates that the Nb atoms of the catalyst 3 exist in the one-atomic layer-structure on SiO₂. Thus, also from the EXAFS study, we propose a unique amorphous one-atomic layer state for the niobium oxide phase attached on SiO₂. The one-atomic layer niobium oxide catalyst 3 showed a Lewis acidity from IR spectra of adsorbed pyridine (1450, 1604 cm⁻¹).

The SiO₂-attached amorphous one-atomic layer niobium oxide catalyst 3 was active for ethanol dehydration in the temperature range 373-573 K. The selective formation of C₂H₄ at the initial stage over the monolayer-Nb catalyst 3 was observed in the whole temperature range, whereas both C₂H₄ and (C₂H₅)₂O were produced over the conventional Nb catalyst as shown in Table 1. The impregnation Nb/SiO₂ catalyst showed a similar

trend in selectivity to an active Al₂O₃ which is a Lewis-acid catalyst, that is, at lower temperatures (C₂H₅)₂O was mainly produced and C₂H₄ was the main product at higher temperatures. Nb₂O₅ (obtained from Wako Kagaku, reagent grade) was less active and gave three kinds of products showing a more heterogeneous property. The active sites of the monolayer catalyst 3 for ethanol dehydration are Lewis

acid sites which are generated from the two-dimensional amorphous structure. Only one ethanol molecule may adsorb on a Lewis acid site to result in the intramolecular dehydration.

The Pt catalyst supported on the amorphous niobium oxide one-atomic layer spread on SiO₂ showed no SMSI phenomenon⁵⁾ unlike a usual Nb₂O₅-supported Pt catalyst.⁶⁾ The amorphous metal-oxide one-atomic layer catalyst may provide a new class of catalysts which show unique catalytic properties.

We wish to express our thanks to Prof. H. Kuroda and Dr. N. Kosugi of the University of Tokyo for their help in the EXAFS analysis using the computer program of Research Center for Spectrochemistry of the University of Tokyo.

Table 1. The activities and selectivities of the three types of niobium oxide catalysts for ethanol dehydration

Sample		Initial rate / 10 ⁻⁵ mol min ⁻¹ g-Nb ⁻¹			
		373 K	430 K	473 K	573 K
One-atomic Layer niobium Oxide	C ₂ H ₄	1.9	3.9	5.9	10.6
	(C ₂ H ₅) ₂ O	0.0	0.0	0.0	0.0
	CH ₃ CHO	0.0	0.0	0.03	0.1
Impreg. Niobium Oxide	C ₂ H ₄	0.5	1.1	1.5	2.4
	(C ₂ H ₅) ₂ O	0.6	0.9	1.1	1.2
	CH ₃ CHO	0.0	0.0	0.0	0.0
Nb ₂ O ₅	C ₂ H ₄	0.014	0.024	0.042	0.12
	(C ₂ H ₅) ₂ O	0.0016	0.0024	0.042	0.098
	CH ₃ CHO	0.015	0.022	0.029	0.038

The initial pressure of C₂H₅OH = 1.1 kPa.

References

- 1) Preliminary reports of this work have already appeared in the abstract of the 50th annual meeting of the Chemical Society of Japan (April, 1985), part I, p.681 and also in *Shokubai*, 27, 371(1985).
- 2) B. M. Gatehouse and A. D. Wadslery, *Acta Crystallogr.*, 17, 1545(1964); K. Kato, *Acta Crystallogr.*, Sect. B, 32, 764(1976); K. Kato and S. Tamura, *ibid.*, 31, 673(1975).
- 3) T. Iizuka, K. Ogasawara, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, 56, 2927(1983); Z. Chen, T. Iizuka, and K. Tanabe, *Chem. Lett.*, 1984, 1085.
- 4) E. I. Ko, R. Bafrafi, N. T. Nuhfer, and N. J. Wagner, *J. Catal.*, 95, 260(1985).
- 5) K. Asakura and Y. Iwasawa, to be published.
- 6) S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 100, 170(1978).

(Received March 7, 1986)