Preparation and Catalytic Properties of a New SiO_2-attached Nb-dimer Catalyst: Regulation of Acidity–Basicity by the number of Metal Atoms in Surface Active Sites

Nobuyuki Ichikuni, Kiyotaka Asakura and Yasuhiro Iwasawa*

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

New Nb dimers on an SiO_2 surface, prepared from the reaction between $[Nb(\eta^5\text{-}C_5H_5)H\text{-}\mu\text{-}(\eta^5, \eta^1\text{-}C_5H_4)]_2$ and surface OH groups, are found to have an oxygen-bridged dimeric structure, as characterised by extended X-ray fine structure (EXAFS), which is active and selective for the dehydration of ethanol in contrast to the dehydrogenation ability of the Nb monomer catalyst.

Chemically designed surfaces active for a particular reaction provide basic information on essential factors for the genesis of solid catalysis and hence developments of new catalytic systems.[1–5] The SiO_2-attached niobium-monomer catalyst prepared by using $Nb(\eta^3\text{-}C_3H_5)_4$ has been found to be the first active Nb sample for the dehydrogenation of ethanol.[6,7] This article reports the preparation of a new SiO_2-attached Nb-dimer catalyst which was characterised by EXAFS, and the change in acid/base catalytic properties by the nucleation of one Nb atom to two Nb atoms in active structures.

The dimeric Nb complex $[Nb(\eta^5\text{-}C_5H_5)H\text{-}\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)]_2$ **1**[8] was synthesized from the reaction of niobocene dichloride with sodium hydride in water-free tetrahydrofuran in a similar way to that previously reported.[9] SiO_2 (Aerosil 200) pretreated at 673 K was immersed in a toluene solution of **1** to react the complex with the surface OH groups at 303 K under strictly oxygen-free conditions, followed by evacuation to remove the solvent. All these procedures were carried out under high purity Ar(99.9999%), since the dimeric complex **1** and particularly the surface dimer **2** are very sensitive to oxygen and moisture. The attached-Nb dimer obtained was treated with H_2 at 823 K and O_2 at 773 K to make the oxidised catalyst **4** as shown in Fig. 1. The evolution of an almost quantitative amount of hydrogen during the preparation of **2** was detected by quadrupole mass spectroscopy (QMS). Moreover, a decrease in the intensity of the IR peak for the OH groups on SiO_2 was observed. This suggests that the attachment proceeded between the hydride of **1** and the surface OH groups on SiO_2. The EXAFS analysis indicated the existence of Nb–O bonding in **2** at *ca.* 0.199 nm with a coordination number of 0.9.

The dimeric complex **1** has two kinds of cyclopentadienyl ligands on each Nb atom as determined by X-ray crystallography[8] (Fig. 1). These two ligands are expected to have different bond strengths to the Nb atom. In fact, the temperature programmed desorption (TPD) spectrum showed two peaks for the evolution of cyclopentadiene at 480 and 570 K with the same peak areas. The number of cyclopentadienyl ligands per Nb atom in **2** was determined to be 1.9–2.0 as shown in Table 1. These results suggest that the structure of **2** is similar to that of the original complex **1** except for the loss of the hydrides. However, the EXAFS analysis revealed a distance of 0.332 nm for Nb–Nb bond, which is much longer than the 0.311 nm for **1**. The species **3** was oxidised to form the catalyst **4** with O_2 at 773 K with the uptake of a quantitative amount of O_2 per Nb atom as shown in Table 1; the amount of the consumed O_2 was determined by taking into

Table 1 Characterization of the Nb dimers on SiO_2

Nb content on SiO_2/wt%	0.1–1.0
Number of cyclopentadienyl ligands per Nb	1.9–2.0
Consumption of O_2 per Nb in step **3** → **4**	0.7–0.75
CT band of **4**/nm	227

EXAFS analysis for **4**

Bond	C.N.[a]	r/nm	DW[b]/nm
Nb=O	0.6	0.179	0.008
Nb–O	1.9	0.193	0.005
Nb–O	1.1	0.213	0.005
Nb–Nb	0.9	0.303	0.006
Nb–Si	2.3	0.328	0.003

[a] Coordination number (± 0.2 ~ 0.5). [b] Debye–Waller factor.

Table 2 Activities and selectivities of Nb/SiO_2 catalysts for the dehydration and dehydrogenation of ethanol[a]

Catalyst	React. temp./K	Initial rate[b] (i)	(ii)	Selectivity/% Ethene	Et_2O	MeCHO
Nb dimer **4**						
	523	0.01	0.17	31.0	63.9	5.1
	548	0.01	0.39	45.0	52.7	2.3
Nb monomer[c]						
	523	1.20	0.05	2.8	1.1	96.1
Impreg. cat.						
1[d]	523	0.05	0.12	26.0	45.3	28.6
2[e]	523	0.01	0.08	27.2	59.8	13.0

[a] Initial pressure of ethanol: 3.3 kPa. [b] mmol min^{-1} g-Nb^{-1}, (i) dehydrogenation, (ii) dehydration. [c] Initial pressure of ethanol: 3.1 kPa. [d] Nb/SiO_2 = 0.45wt%. [e] Nb/SiO_2 = 0.92wt%.

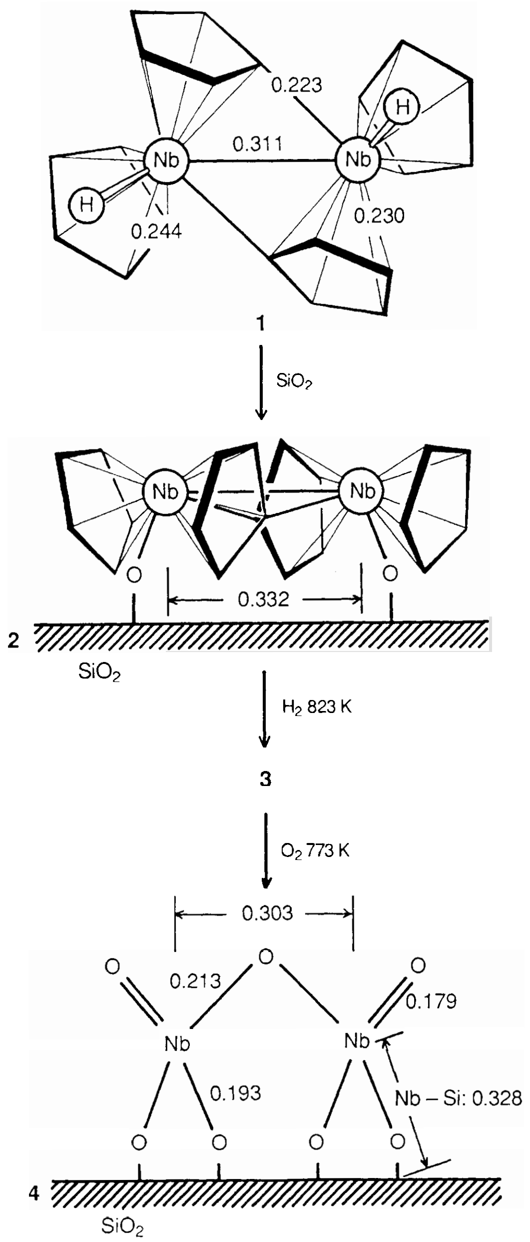

Fig. 1 Preparation steps and structures for the Nb-dimers on SiO_2. Bond distances (nm).

account the formation of CO_2 from the surface residual carbon. The charge transfer (CT) band of $Nb^{5+}{=}O^{2-}$ in species **4** observed at 227 nm may exclude the possibility of octahedral symmetry (*cf.* octahedral Nb_2O_5: 310 nm). The Nb K-edge XANES spectrum of **4** showed a definite 1s→4d transition peak, suggesting a tetrahedral symmetry.

The curve-fitting analysis[10] for the Nb K-edge EXAFS data of **4** was performed by using empirical parameters extracted from Nb foil, $LaNbO_4$ and $NbSi_2$ for Nb–Nb, Nb–O and Nb–Si bonds, respectively. The curve-fitting results for the catalyst **4** are shown in Table 1. The catalyst **4** showed the Nb–Nb bond at a distance of 0.303 nm with a coordination number of 0.9 and the Nb–O bond at a distance of 0.213 nm with a coordination number of 1.1, suggesting the oxygen-bridged dimer structure **4** in Fig. 1. Besides these bonds, Nb–O(surface) and Nb–Si bonds were observed at distances of 0.193 and 0.328 nm, respectively, which are similar to the bond lengths for the Nb monomers on SiO_2. Furthermore, the Nb=O double bond at a distance of 0.179 nm was observed in agreement with the observation of the CT band.

The catalytic dehydration and dehydrogenation of ethanol were carried out in the temperature range 473–523 K. The Nb monomer catalyst exhibited high activity and selectivity for the dehydrogenation to produce acetaldehyde[6,7] indicating the basic character of the Nb monomers. However, the Nb dimer catalyst showed high selectivity for dehydration to form diethyl ether and ethene, as shown in Table 2, where the dehydrogenation was markedly suppressed and the dehydration was promoted, indicating the acidic character of the Nb dimers. The catalytic features of the Nb monomers and dimers were independent of the Nb loadings in the range 0.10–2.0 wt%, suggesting a nearly homogeneous distribution of Nb sites. The conventionally impregnated Nb catalyst was less active and unselective. It is to be noted that the change of the number of Nb atoms in active sites from one to two gave rise to the complete reverse of basicity–acidity in catalytic properties.

Received, 3rd October 1990; Com. 0/04442C

References

1 Yu. I. Yermakov, B. N. Kuznetsov and V. A. Zakharov, in *Catalysis by Supported Complexes*, Elsevier, Amsterdam, 1981.
2 Y. Iwasawa, ed., *Tailored Metal Catalysts*, Reidel, Dordrecht, Holland, 1986.
3 Y. Iwasawa, *Adv. Catal.*, 1987, **35**, 187.
4 F. R. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht, Holland, 1985.
5 B. C. Gates, L. Guczi and H. Knözinger, in *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986.
6 M. Nishimura, K. Asakura and Y. Iwasawa, *J. Chem. Soc., Chem. Commun.*, 1986, 1660.
7 M. Nishimura, K. Asakura and Y. Iwasawa, *Proc. 9th Intern. Congr. Catal. Calgary*, 1988, vol. 4, p. 1842.
8 L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 1971, **93**, 5924.
9 D. A. Lemenovskii, I. F. Urazowski, I. E. Nifant'ev and E. G. Pervalova, *J. Organomet. Chem.*, 1985, **292**, 217.
10 B. K. Teo, *EXAFS, Basic Principles and Data Analysis*, Springer-Verlag, Berlin, 1986.