

New SiO₂-supported Niobium Monomer Catalysts for Dehydrogenation of Ethanol

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New Nb^V monomers supported on SiO₂, Al₂O₃, or TiO₂ have been prepared by reaction between Nb(η³-C₃H₅)₄ and the surface OH groups of SiO₂, Al₂O₃, or TiO₂, followed by treatment with H₂ and O₂; of these the SiO₂-supported Nb catalyst shows high activity and selectivity for the dehydrogenation of ethanol to give acetaldehyde at 473–573 K unlike the preferential dehydration observed over the usual Nb impregnation catalysts.

The use of suitable organic complexes of transition metals provides a potential method for the synthesis of tailored metal catalysts with well-defined structures, electronic states, and active site environments which possess great advantages over conventional impregnation catalysts.¹ Niobium oxide catalysts have been studied largely from the view-points of support effects on metal catalysis or acidic properties.² We report the preparation of new niobium(v) monomers supported on SiO₂, Al₂O₃, and TiO₂ and the high activity and selectivity of particularly the SiO₂-supported Nb catalyst for the dehydrogenation of ethanol to give acetaldehyde.

The supported Nb^V catalysts (7)–(9) were prepared *via* the surface complexes (1)–(3) which were obtained by the reaction between Nb(η³-C₃H₅)₄³ and surface OH groups of SiO₂ (Aerosil-200, pretreated at 673 K), Al₂O₃ (Alon-C, at 773 K), and TiO₂ (P-25, at 473 K) at 233–273 K, followed by treatment with H₂ and O₂ as illustrated in Scheme 1. The number and character of C₃H₅ ligands and the oxidation states of Nb in the species (1)–(3) were determined by chemical analysis, and i.r. and e.s.r. (10 line hyperfine structure derived from 9/2 spin of Nb^{IV}) spectrometry as shown in Table 1. The C₃H₅ ligands (σ-type character) of the species (1)–(3) were removed by H₂ reduction to give rise to the lower-valent Nb ions (4)–(6). The species (4)–(6) were oxidized to the Nb^V state with O₂ at 673 K, with uptake of a quantitative amount of oxygen as shown in Table 1; the amount of consumed O₂ was determined by taking into account the formation of CO₂ from residual surface carbons. The binding energies of Nb 3d levels (3d_{3/2} and 3d_{5/2}) of the samples (7)–(9) in Table 1 were nearly the same as or higher than those of Nb₂O₅ (208.9, 206.0 eV), indicating that the Nb ions of (7)–(9) are genuinely in a

pentavalent state. Conversely, the structures (4), (5), and (6) are proposed to be in 1+, 1+, and 3+ states, respectively. The Raman shift of (7) appeared at 880 cm⁻¹ which is close to 850 cm⁻¹ for tetrahedral YNbO₄⁴ rather than the peak at 980 cm⁻¹ for octahedral Nb₂O₅. The charge transfer (CT) band of Nb⁵⁺=O²⁻ observed at 235 or 220 nm for (7) or (8), respectively, may also exclude the possibility of octahedral symmetry (*cf.* octahedral Nb₂O₅; 310 nm). The X-ray absorption near-edge structure spectrum of (8) exhibited a distinct peak assignable to the 1s→4d transition of Nb^V ions in a near tetrahedral symmetry. The TiO₂-supported Nb species (9) showed a Raman peak at 840 cm⁻¹ which is similar to 850 cm⁻¹ of YNbO₄, while the CT band of (9) was observed at 285 nm in between tetrahedral (220–235 nm) and octahedral (310–350 nm) symmetry. This suggests that Nb^V ions of (9) are situated in a different bond-arrangement from the structures (7) or (8) as expected from Scheme 1.

The bond distances and numbers of the structures (7)–(9) were determined by a curve-fitting analysis of the Nb K-edge EXAFS data obtained by use of synchrotron radiation as illustrated in Scheme 1. The EXAFS analysis showed the presence of the Nb–Si(surface) or the Nb–Ti(surface) bonds for the structures (7) or (9), respectively, besides the Nb=O and Nb–O bonds. The structure (9) agrees well with bonding on the (100) face of TiO₂(anatase). The Nb^V monomers (7)–(9), distributed as isolated species, are entirely different in structure from the Nb species in conventional Nb impregnation catalysts which include agglomerated Nb species as proved from the observation of Nb–Nb bonds.

The dehydrogenation and dehydration of ethanol to give acetaldehyde and diethyl ether or ethene over the catalysts

Table 1. Properties and characterization of the surface Nb species (1)–(9).

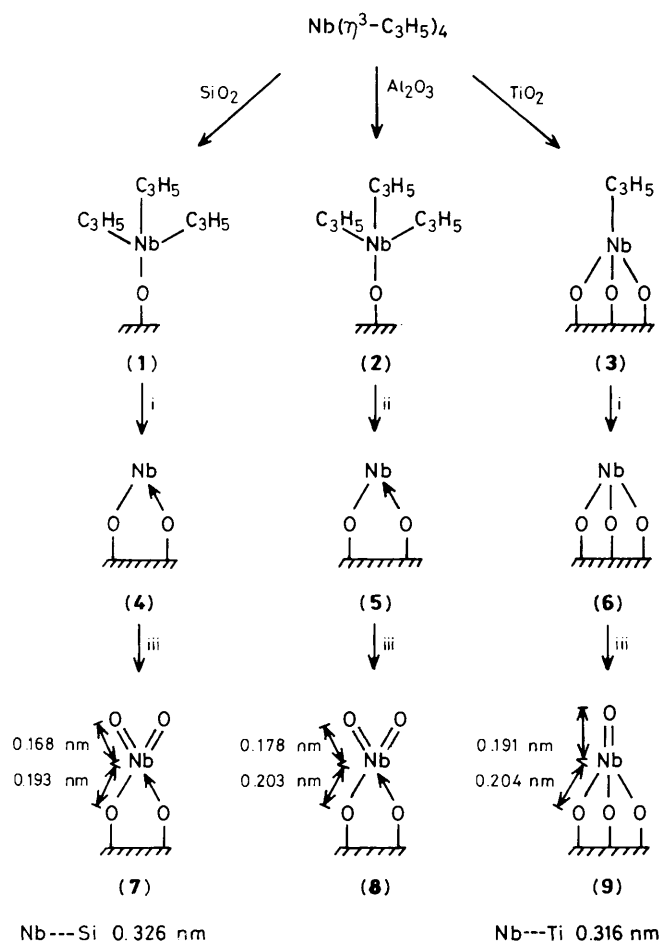
	SiO ₂	Al ₂ O ₃	TiO ₂
Nb content on support/wt%	2.0	2.3	2.1
Number of C ₃ H ₅ ligands per Nb atom in (1), (2), and (3)	3.0	2.8	0.9
E.s.r. data for (1), (2), and (3)	<i>g</i> = 1.98, <i>g</i> = 2.01 <i>A</i> = 210 G, <i>A</i> = 50 G ^a	<i>g</i> = 1.99 <i>A</i> = 220 G	—
I.r. peaks for (1), (2), and (3)			
ν _{C–H} /cm ⁻¹	3084	3078	3080
ν _{C–C} /cm ⁻¹	1641	1641	1641
Consumption of O ₂ per Nb atom in the steps (4)→(7), (5)→(8), and (6)→(9)	1.1	1.1	0.6
XPS binding energies of Nb in (7), (8), and (9)/eV ^b			
3d _{3/2}	209.8	208.8	208.8
3d _{5/2}	206.8	206.2	205.8
Raman shifts of (7), (8), and (9)/cm ⁻¹	880	—	840
CT bands of (7), (8), and (9)/nm	235	~220	285

^a 1 G = 10⁻⁴ T. ^b XPS = X-ray photoelectron spectroscopy.

Table 2. Activities and selectivities of various Nb catalysts in the dehydrogenation of ethanol.^a

Catalyst	Reaction temp./K	Initial rate ^b	Turnover frequency ^c	% Selectivity		
				Acetaldehyde	Ethene	Diethyl ether
(7)	523	1.25	0.116	96.1	2.8	1.1
	548	1.66	0.154	93.2	6.1	0.7
	573	3.17	0.296	84.4	13.7	1.9
(8)	523	4.03	0.374	4.6	5.7	89.7
	548	5.33	0.495	4.1	19.6	76.3
	573	11.78	1.084	3.4	26.9	69.7
(9)	523	0.22	0.020	79.0	6.6	14.4
	548	0.55	0.051	61.9	15.2	22.9
	573	1.74	0.162	66.6	11.0	22.4
Impreg.Nb/SiO ₂	523	0.22	0.020	41.2	22.5	36.3
	548	0.43	0.040	16.2	34.6	49.2
	573	0.81	0.075	2.7	59.2	38.1
Nb ₂ O ₅ ^d	523	2.05 × 10 ⁻⁵	1.90 × 10 ⁻⁶	68.3	16.2	15.5
	573	8.43 × 10 ⁻⁵	7.83 × 10 ⁻⁶	32.2	40.7	27.1

^a EtOH: 3.1 kPa. ^b In mol min⁻¹ (g Nb)⁻¹. ^c In product-molecules min⁻¹ (Nb atom)⁻¹. ^d Commercially obtained from Wako Pure Chemical Industries Ltd., 99.5%.



Scheme 1. The attachment of Nb(η³-C₃H₅)₄ onto SiO₂, Al₂O₃, and TiO₂ and surface transformations. i, H₂, 673 K; ii, H₂, 773 K; iii, O₂, 673 K.

(7)–(9) were investigated in a closed circulating system in the temperature range 473–573 K. The SiO₂-supported Nb catalyst (7) was found to be the first Nb sample which exhibited a high activity and selectivity for the dehydrogenation of ethanol as shown in Table 2. Acetaldehyde and hydrogen were stoichiometrically produced during the dehydrogenation. On the other hand, over the usual Nb impregnation catalyst, dehydration to form ethene and diethyl ether occurred predominantly. Nb₂O₅ was much less active for these reactions. The Nb monomers (9) supported on TiO₂ produced mainly the dehydrogenated product but with lower activity and selectivity compared with catalyst (7). On the Al₂O₃-supported species (8) dehydrogenation was prevented by a high dehydration activity, where acidic sites of Al₂O₃ neighbouring the Nb ions may play a role in the dehydration. The reaction mechanism for the dehydrogenation on the new active Nb monomer catalyst (7)⁵ was entirely different from the dehydrogenation mechanism on the Mo monomer catalyst with a similar structure for the active species.

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