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Carbon Monoxide Hydrogenation on SiO_2-, Al_2O_3-, or TiO_2-Attached Nb-Monomer Catalysts

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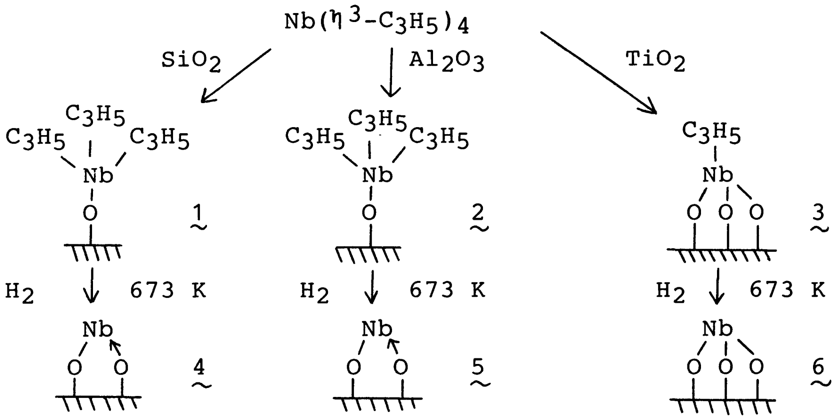
The new low-valent Nb monomer catalysts which were prepared by taking advantage of the reaction between $Nb(\eta^3\text{-}C_3H_5)_4$ and surface OH groups on SiO_2, Al_2O_3, or TiO_2, followed by the treatments with H_2, were found to be active for the hydrogenation of carbon monoxide in which C_2-C_4 hydrocarbons were mainly produced in the temperature range 423-598 K. In contrast, only the disproportionation reaction of CO to form CO_2 proceeded on usual impregnation Nb catalysts and Nb_2O_5.

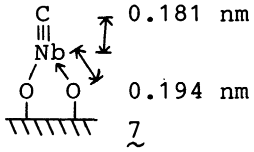
The attached metal catalysts obtained by the reactions between metal-η^3-C_3H_5 complexes and surface OH groups of inorganic oxides such as SiO_2, Al_2O_3, etc., followed by chemical treatments with H_2 or O_2, have been demonstrated to provide a new way of preparations of active, well-defined catalysts[1)] with new surface structures and hence novel catalytic properties.[2,3)] This attaching method may also be useful particularly for preparations of highly dispersed, lower-valent metal atoms which are hardly obtained in a traditional way (impregnation using inorganic metal salts, calcination in air and reduction with H_2 or CO). Niobium in Nb_2O_5 and impregnated Nb(V) catalysts is a hardly-reduced element and the study on their catalysis has been restricted to higher-valent Nb catalysts although NbO_x ($x<2.5$) species has been suggested to contribute to the catalysis of Nb_2O_5-supported metal catalysts in a strong metal-support interaction (SMSI) state.[4-7)] In the present paper the catalytic properties of the low-valent Nb monomers attached on SiO_2, Al_2O_3, or TiO_2 in the hydrogenation of CO are reported.

The low-valent Nb catalysts (**4**-**6**) were prepared by the treatments of the attached Nb(IV)-allyl catalysts[2)] (**1**-**3**) with H_2 at 673 K as shown in Scheme 1. The surface structures **1**-**3** have been characterized by means of ESR, IR, temperature programmed decomposition, and chemical analysis.[2)] The allyl ligands in **1**-**3** were removed by the H_2 reduction, evolving C_1-C_4 hydrocarbons (mainly CH_4, C_2H_6, and C_3H_8). After the H_2 treatments the characteristic ESR peak for Nb(IV) ions in **1**-**3** disappeared, suggesting that the Nb(IV) species were reduced to the lower valent level. The species **4**-**6** were converted to Nb(V) monomers by oxidation with O_2, uptaking two O atoms or one O atom per Nb atom for **4** and **5**, or **6**, respectively, as previously reported.[3,8)] The Nb(V) monomers were found to be attached to the support surfaces in a bidentate form (SiO_2 and Al_2O_3) or a terdentate form (TiO_2)



Scheme 1. The attachment of Nb(η^3-C_3H_5)$_4$ onto SiO_2, Al_2O_3, and TiO_2, and the surface transformations.

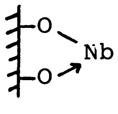
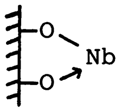
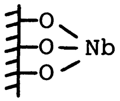
by means of EXAFS, UV, and Raman spectroscopies.[3] Reversely, from the Nb(V) structures the Nb(I) or Nb(III) structures in Scheme 1 may be suggested. However, judging from the CO_2 formation in the oxidation of 4 and 5 with O_2, more than one carbon atoms per Nb atom still remained on the catalysts 4 and 5 after the H_2 treatments of 1 and 2 at 673 K, respectively. In order to know whether or not these residual carbons are chemically bound to Nb atoms, the EXAFS spectra of 1 and 4 as typical examples were measured at 77 K. The Fourier transform of the EXAFS spectrum of 1 showed a peak assignable to Nb-C and Nb-O bonds which could not be distinguished each other. The bond distance and the coordination number were determined to be 0.190 ± 0.003 nm and 3 ± 1, respectively, by a curve-fitting technique. The Fourier transform of the EXAFS spectrum of 4 also showed one peak. However the one-shell curve-fitting analysis resulted in a rather large Debye Waller factor, suggesting that this peak may not be composed of a single coordination shell. Then we carried out the two-shell fitting analysis and obtained much better results. The bond distances (the coordination numbers) were found to be 0.181 ± 0.003 nm(0.7 ± 0.3) and 0.194 ± 0.003 nm(1.7 ± 0.5). The longer-bond peak is straightforwardly assigned to Nb-O (surface) bonds from the similarity in bond length to the Nb-O bonds of 1 (0.190 nm) and the SiO_2-attached Nb(V) monomer structure (0.193 nm). The bond distance of 0.181 nm is much shorter than 0.190 nm for the Nb-C (σ- allyl) bonds and the Nb-O (surface) bonds and also much longer than 0.168 nm for the Nb=O double bond of the Nb(V) monomer structure. Hence, these results together with the presence of the residual carbons on 4 suggest that the shorter- bond peak is assignable to the Nb-C(carbide) bond. The EXAFS analysis showed no Nb-Nb bond, which confirms the monomer structure of 4. Thus the Nb-carbide monomer (7) attached to SiO_2 through two oxygen atoms is proposed. In contrast to 4/SiO_2 and 5/Al_2O_3 the amount of the residual carbons on 6/TiO_2 was less than 0.1 C/Nb.



7

The hydrogenation of carbon monoxide on the attached Nb catalysts 4-6, the impregnation Nb catalysts, and an unsupported Nb_2O_5 was carried out in a closed circulating system (dead volume: 170 cm^3) equipped with a U-shaped liq. N_2 trap. The reaction rates and selectivities were mesured in 1.5 h of reaction.

Table 1. The hydrogenation of CO over the attached Nb catalysts, the impregnation Nb catalysys, and Nb_2O_5

Catalysts	Supports	Reaction temperatures / K	Reaction rates / µmol•min^{-1} •(g-Nb)$^{-1}$	Selectivities / %								
				CO_2	C_1	C_2		C_3		C_4		C_5
						C_2^-	$C_2^=$	C_3^-	$C_3^=$	C_4^-	$C_4^=$	
	SiO_2	423	23.4	0	10	36	0	27	1	17	0	9
		473	27.6	0	19	33	0	24	5	13	0	6
		523	30.6	0	16	41	0	23	4	11	0	5
		573	34.8	0	14	39	3	12	26	3	3	0
Impreg.	SiO_2	523	3.6	100	0	0	0	0	0	0	0	0
	Al_2O_3	473	4.8	0	37	14	1	33	7	8	0	0
		498	10.2	0	41	17	0	30	5	7	0	0
		523	16.2	0	65	14	0	14	2	5	0	0
		548	22.8	0	74	6	5	5	8	0	2	0
		598	52.2	0	55	2	26	3	11	0	3	0
Impreg.	Al_2O_3	523	4.8	100	0	0	0	0	0	0	0	0
	TiO_2	423	4.8	0	11	31	0	36	0	22	0	0
		498	9.6	0	16	41	0	22	5	16	0	0
		548	14.4	0	27	33	0	16	10	8	6	0
		598	19.8	0	30	18	0	7	29	1	15	0
Impreg.	TiO_2	523	19.8	100	0	0	0	0	0	0	0	0
Nb_2O_5	none	523	0.6	100	0	0	0	0	0	0	0	0

CO = 13.3 kPa, H_2 = 26.7 kPa.

The products of CO hydrogenation on the attached catalysts were hydrocarbons (100% selectivity for C_1-C_5) in the temperature range 423-598 K as given in Table 1. No formation of CO_2 was observed. The SiO_2-attached Nb catalyst 4 was found to show the highest activity among the three catalysts 4-6. It yielded mainly C_2-C_4 hydrocarbons with the selectivities of 75-86% at 423-573 K. As the reaction temperature increased, the formation of unsaturated hydrocarbons relatively increased; especially propene attained to 68% of C_3 components. Besides this feature, the selectivity to methane was kept to the low levels, 10% (423 K) - 14% (573 K). The activities of the TiO_2-attached Nb catalyst 6 was lower than those of the SiO_2-attached Nb catalyst 4 as shown in Table 1. The catalyst 6 also yielded mainly C_2-C_4 hydrocarbons with the selectivities of 70-89% which are similar to those for 4, but the C_4 formation was larger on 6 than on 4. In contrast to 4 and 6, methane was preferentially produced on 5. The unsaturated hydrocarbons became main products in C_2-C_4 components at the higher temperatures. The trend that the formatiom of C_2-C_4 alkenes increased with an increase of reaction temperature may be a specific feature of the low-valent Nb monomer catalysts.

On the other hand, an unsupported Nb_2O_5 and conventional impregnation Nb catalysts which were prepared by a usual impregnation method using a methanol solution of $NbCl_5$, followed by calcination at 820 K, poduced CO_2 alone under the similar conditions as shown in Table 1. The results were similar also to the catalysts reduced with H_2 at 673 K or 820 K in situ before CO hydrogenation.

The attached Nb catalysts 4-6 were stable during CO hydrogenation and showed constant activities for at least 5 h. This may be peculiar since the catalysts 4 and 5 have formally univalency which should be oxidized and poisoned by oxygen atoms from CO and water formed during catalysis. The carbide ligand shown in 7 is likely to prevent the active Nb structure from unfavorable oxidation and hence deactivation. The carbide (^{12}C) ligand was not an active precursor for the reaction because ^{13}CO hydrogenation on 7 produced the hydrocarbons containing only ^{13}C . The attached catalyst 6 had almost no carbon as the ligand of Nb but in this case the Nb atoms are already in a moderate oxidation state of tervalency. Although the working Nb structures for CO hydrogenation are under a further investigation, the low valent niobia were found to serve as an active element for CO hydrogenation.

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8) The amounts of oxygen consumed in the oxidation of 4-6 to the Nb(V) structures were determined by taking into account the amounts of CO_2 formed from the oxidation of the residual carbons.

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