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$Nb_2O_5 \cdot nH_2O$ as a Heterogeneous Catalyst with Water-Tolerant Lewis Acid Sites

Kiyotaka Nakajima,[†,#] Yusuke Baba,[†] Ryouhei Noma,[†] Masaaki Kitano,[†] Junko N. Kondo,[‡]
Shigenobu Hayashi,[§] and Michikazu Hara*[,†,#]

[†]Materials and Structures Laboratory and [‡]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

[§]Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

[#]Kanagawa Academy of Science and Technology, 3-2-1 Sakado, Takatsu-ku, Kawasaki 213-0012, Japan

S *Supporting Information*

ABSTRACT: Niobic acid, $Nb_2O_5 \cdot nH_2O$, has been studied as a heterogeneous Lewis acid catalyst. NbO_4 tetrahedra, Lewis acid sites, on $Nb_2O_5 \cdot nH_2O$ surface immediately form $NbO_4{-}H_2O$ adducts in the presence of water. However, a part of the adducts can still function as effective Lewis acid sites, catalyzing the allylation of benzaldehyde with tetraallyl tin and the conversion of glucose into 5-(hydroxymethyl)furfural in water.

Lewis acids function as catalysts for the formation of C−C bonds in organic compounds,[1] and therefore the chemical industry utilizes large amounts of Lewis acid catalysts, such as $AlCl_3$, BF_3, and transition metal halides, for the production of industrially important chemicals. However, these homogeneous catalysts decompose or are ineffective in water, an environmentally benign solvent, and have serious drawbacks such as the production of waste, hazards of handling, separation from products, and corrosion of equipment. In addition, the recovery and reuse of homogeneous Lewis acid catalysts is an extremely formidable obstacle. Any heterogeneous Lewis acid catalysts that are insoluble, easily separable from products, and highly active in water would be applicable for environmentally benign chemical production. Rare earth metal triflates, which are homogeneous Lewis acids, exhibit excellent catalytic activity and selectivity for various organic reactions, even in the presence of water,[2] and polymer or inorganic oxide-supported rare earth metal triflates have been developed as heterogeneous Lewis acids.[3] While it is well-known that many inorganic oxides including zeolites and metal oxides have Lewis acid sites, these have generally been regarded as inactive sites for reactions in water, due to the formation of Lewis acid−base adducts by the coordination of water to the Lewis acid sites. We have focused on niobic acid, $Nb_2O_5 \cdot nH_2O$, as a potential solid Lewis acid candidate with activity in water. $Nb_2O_5 \cdot nH_2O$ is readily prepared by the hydrolysis of $NbCl_5$ or $Nb(OC_2H_5)_5$ and is an amorphous metal oxide composed mainly of distorted NbO_6 octahedra and NbO_4 tetrahedra, as shown in Figure S1.[4] Nb−O bonds are highly polarized in these distorted polyhedrons, so that a part of the surface OH groups function as Brønsted acid sites.[4,5] While NbO_4 tetrahedra function as Lewis acid sites, they have been considered not to function in water.[6] However, it has been reported that water molecules are coordinated to $Yb(OSO_2CF_3)_3$ ($Yb(OTf)_3$), a rare earth metal triflate highly polarized by OSO_2CF_3 groups, during reaction in water, and this homogeneous catalyst functions as an efficient Lewis acid in water, despite the coordination of water.[2] This suggests that Lewis acid sites in a highly polarized field such as the NbO_4 tetrahedra in $Nb_2O_5 \cdot nH_2O$ can function even in water.

Fourier transform infrared (FT-IR) and Raman spectroscopies were used to investigate the Lewis acid sites on $Nb_2O_5 \cdot nH_2O$ in the presence of water. The Raman spectrum for $Nb_2O_5 \cdot nH_2O$ powder dehydrated at 423 K in Figure 1 shows vibrational bands at 550−750, 800−900, and 988 cm^{-1} that are attributable to Nb−O−Nb, NbO_6 octahedra, and NbO_4 tetrahedra, respectively.[6,7] Exposure of dehydrated $Nb_2O_5 \cdot nH_2O$ (BET surface area: 179 m^2 g^{-1}, Brønsted acid amount: 0.17 mmol g^{-1}, Lewis acid amount: 0.15 mmol g^{-1}, see the Supporting Information [SI]) to water vapor diminishes the band at 988 cm^{-1}, which indicates that NbO_4 tetrahedra are present only on the $Nb_2O_5 \cdot nH_2O$ surface and $NbO_4{-}H_2O$ adducts are immediately formed in the presence of water. When water-adsorbed $Nb_2O_5 \cdot nH_2O$ is dehydrated at 423 K, the band at 988 cm^{-1} appears again. Such reversibility between NbO_4 tetrahedra and $NbO_4{-}H_2O$ adducts is not observed in isolated NbO_4 on other metal oxide surfaces.[7] Differential FT-IR spectra for CO-adsorbed dehydrated $Nb_2O_5 \cdot nH_2O$ are presented in Figure. 2a where CO is employed as a basic probe molecule. The intensities of the three bands at 2145, 2168, and 2188 cm^{-1}, assignable to physisorbed CO and CO adsorbed on Brønsted and Lewis acid sites,[8] respectively, increase with the amount of introduced CO, and the band intensities due to acid sites reach plateaus at $P_{co} > 4.8$ kPa. Figure 2b shows the results for CO-adsorption experiments on hydrated $Nb_2O_5 \cdot nH_2O$ with 3.0 mmol of H_2O adsorbed on 1 g of sample. Assuming the adsorption cross section area of a H_2O molecule is 0.125 nm^2, then 1.3 layers of H_2O would be adsorbed on the sample. Raman spectroscopy confirmed that most of the NbO_4 tetrahedra form $NbO_4{-}H_2O$ adducts under the experimental conditions; however, the band due to CO adsorbed on

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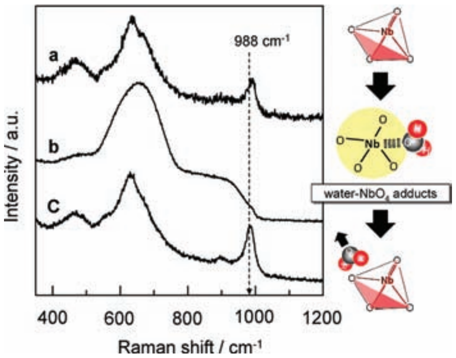


Figure 1. Raman spectra of $Nb_2O_5 \cdot nH_2O$ in a quartz cell. (a) $Nb_2O_5 \cdot nH_2O$ evacuated at 423 K for 2 h to remove water. (b) Sample (a) exposed to saturated water vapor at 300 K for 3 h. (c) Sample (b) evacuated at 423 K for 2 h.

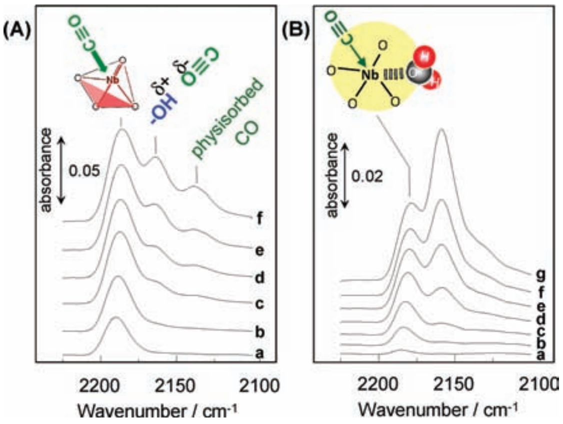
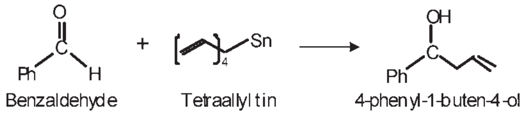


Figure 2. Differential FT-IR spectra for (A) dehydrated and (B) hydrated $Nb_2O_5 \cdot nH_2O$ at 90 K. (A) Prior to CO adsorption, the sample was heated at 423 K for 1 h under vacuum. Gas phase CO pressure: (a) 7.1×10^{-3}, (b) 1.2×10^{-2}, (c) 2.2×10^{-2}, (d) 4.0×10^{-2}, (e) 6.6×10^{-2}, and (f) 1.4×10^{-1} kPa. () Prior to CO adsorption, the sample was dehydrated at room temperature for 24 h under vacuum. Gas-phase CO pressure: (a) 6.1×10^{-3}, (b) 9.3×10^{-3}, (c) 1.4×10^{-2}, (d) 2.6×10^{-2}, (e) 4.3×10^{-2}, (f) 6.8×10^{-2}, and (g) 1.4×10^{-1} kPa.

Table 1. Catalytic Activity for the Allylation of Benzaldehyde with Tetraallyl Tin in Water[a]



	acid density/mmol g^{-1}			
catalyst[b]	BA[c]	LA[d]	SDS/mmol	yield[e] (%)
$Sc(OTf)_3$	–	2.0	0.0	88
			0.3	38
$Nb_2O_5 \cdot nH_2O$	0.17[f]	0.15[f]	0.0	21
	0.14[g]	0.03[g]	0.3	23
$Na^+/Nb_2O_5 \cdot nH_2O$	–	0.17[f]	0.3	21
	–	0.03[g]		

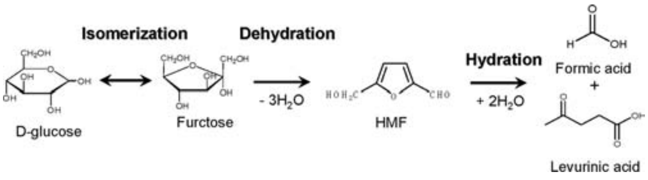
[a] Reagents and conditions: distilled water, 15 mL; benzaldehyde, 0.4 mmol; tetraallyl tin, 0.2 mmol; sodium dodecyl sulfate, 0.3 mmol. [b] 0.1 g. [c] Brønsted acid. [d] Lewis acid. [e] Yield of 4-phenyl-1-buten-4-ol (%) for 1 h. [f] Dehydrated sample. [g] Water-adsorbed sample (see the SI).

Lewis acid sites is observed even on hydrated $Nb_2O_5 \cdot nH_2O$. In addition, it was confirmed that the Lewis acid sites interact with pyridine molecules even on $Nb_2O_5 \cdot nH_2O$ in saturated H_2O vapor, multilayer adsorption of water (see the SI). A part of the Lewis acid sites on $Nb_2O_5 \cdot nH_2O$ are therefore expected to function as water-tolerant active sites. The amount of NbO_4—CO on hydrated $Nb_2O_5 \cdot nH_2O$ was approximately one-fifth of that on dehydrated $Nb_2O_5 \cdot nH_2O$ (see the SI). The vibration (2178—2185 cm^{-1}) of CO bonded to NbO_4 on the hydrated sample is weaker than that of the dehydrated sample (2186—2190 cm^{-1}). This can be attributed to CO lateral interaction with H_2O or dipole—dipole coupling interactions, rather than strong/weak Lewis NbO_4—H_2O adducts.

Such active and inactive NbO_4—H_2O adducts may be attributed to the difference in environment surrounding NbO_4 tetrahedra. There was no significant difference in effective Lewis acid density (on dehydrated and hydrated samples) and catalytic activity (see below) among commercial $Nb_2O_5 \cdot nH_2O$ (supplied by CBMM) and $Nb_2O_5 \cdot nH_2O$ samples prepared by the hydrolysis of $NbCl_5$ or $Nb(OC_2H_5)_5$ at room temperature, suggesting that the NbO_4 tetrahedra resulting in active NbO_4—H_2O adducts as Lewis acid sites are inevitably formed during the formation of $Nb_2O_5 \cdot nH_2O$ although the environment surrounding such NbO_4 tetrahedra has not been clarified yet.

The catalysis of $Nb_2O_5 \cdot nH_2O$ was evaluated through the allylation of benzaldehyde with tetraallyl tin and the conversion of glucose into 5-(hydroxymethyl)furfural (HMF) in water. Allylation in water is catalyzed by water-tolerant homogeneous Lewis acids such as rare earth metal triflates.[2,3] Conversion of glucose, a key component of cellulosic biomass, into HMF is an attractive alternate route to sustainable chemical production; HMF can be further converted into various polymers, synthetic rubbers, plastics and pharmaceuticals.[9] HMF formation from glucose proceeds by isomerization of glucose to fructose, followed by dehydration of fructose in the presence of catalysts. Zhang et al. reported that $CrCl_2$, a homogeneous Lewis acid in ionic liquids, functions as an efficient catalyst for one-step HMF formation under mild reaction conditions (ca. 373 K).[9c] The hydrolysis of cellulosic biomass generally proceeds in water, resulting in an aqueous solution of glucose. Therefore, a catalytic system that could convert glucose into HMF in water, for example, a water-tolerant heterogeneous Lewis acid, would be favorable as a large-scale environmentally benign process. Table 1 summarizes the results for allylation in the presence of the tested catalysts. Sodium dodecyl sulfate (SDS) was used in this experiment as a surfactant, which solubilizes hydrophobic organic reactants and/or forms emulsion in water.[2a] Therefore, the addition of SDS to the reaction system results in a remarkable increase in the catalytic performance of $Sc(OTf)_3$. Na^+-exchanged $Nb_2O_5 \cdot nH_2O$ ($Na^+/Nb_2O_5 \cdot nH_2O$) (see the SI), where the Brønsted acid sites are blocked with Na^+, also catalyzes the reaction as well as $Nb_2O_5 \cdot nH_2O$. Neither dehydrated nor hydrated $Na^+/Nb_2O_5 \cdot nH_2O$ samples have Brønsted acid sites, and the number of the Lewis acid sites on dehydrated and hydrated $Na^+/Nb_2O_5 \cdot nH_2O$ is the same on dehydrated and hydrated $Nb_2O_5 \cdot nH_2O$, respectively, as shown in Table 1. This means that the formation of NbO_4—H_2O adducts does not result in the formation of Brønsted acid sites on $Nb_2O_5 \cdot nH_2O$. FT-IR measurements confirmed that all the Brønsted acid sites

Table 2. Catalytic Activity for the Conversion of Glucose into HMF in Water[a]



catalyst[b]	BA[c]	LA[d]	conv.[e]	selectivity % Fru[f]	HMF	FA[g]	LA[h]	unknown
HCl	9.9	–	100	–		5.7	27.1	65.5
H_2SO_4	22.4	–	100	–		8.4	56.4	35.2
Amberlyst-15	4.8	–	89	–		42.3	42.3	15.4
NafionNR50	0.9	–	65	–		9.8	35.4	54.8
H-mordenite (Si/Al = 90)	1.1	0.26	12	35.2		–	–	64.8
H-ZSM-5 (Si/Al = 90)	0.15	0.05	34	–		3.8	–	96.2
$Nb_2O_5 \cdot nH_2O$	0.17[i] 0.14[j]	0.15[i] 0.03[j]	100	–	12.1	3.2	–	84.6
Na+/ $Nb_2O_5 \cdot nH_2O$	–[i] –[j]	0.17[i] 0.03[j]	100	0.5	12.4	2.5	–	84.6
H_3PO_4/ $Nb_2O_5 \cdot nH_2O$	0.04[i] 0.04[j]	0.11[i] 0.02[j]	92	0.8	52.1	2.6	1.2	43.3

[a] Reagents and conditions: distilled water, 2.0 mL; D-glucose, 0.02 g (0.11 mmol); temperature, 393 K. [b] 0.2 g. [c] Brønsted acid amount (mmol g^{-1}), [d] Lewis acid amount (mmol g^{-1}), [e] Yield conversion (%) for 3 h, [f] Fructose, [g] formic acid, [h] Levulinic acid [i] Dehydrated sample, [j] Water-adsorbed sample (see the SI).

on $Nb_2O_5 \cdot nH_2O$ were blocked with Na^+ (Figure S3, SI), even after the reaction, and they could not function as effective active sites for the reaction. Therefore, the Lewis acid sites appear to be active for the reaction, even in water. The addition of SDS to the reaction system is not effective for increase in catalytic activity of $Nb_2O_5 \cdot nH_2O$. This may be attributed to the adsorption capability of $Nb_2O_5 \cdot nH_2O$ for the reactant molecules without SDS.

Table 2 summarizes the results for the conversion of glucose into HMF in water (393 K). The homogeneous and heterogeneous Brønsted acids (HCl, H_2SO_4, NafionNR50 and Amberlyst-15) produce no HMF but instead yield levulinic and formic acids under reaction conditions. This is due to hydration ability of Brønsted acids in water:[9c] the evolved HMF is rapidly converted into levulinic and formic acids.[9d−g] In contrast, $Nb_2O_5 \cdot nH_2O$ produces HMF yield, and no decrease in activity was observed even after several reuses of the catalyst (Figure S5, SI). Although it has been reported that the conversion of fructose into HMF proceeds in the presence of a small amount of $Nb_2O_5 \cdot nH_2O$ catalyst,[9h,i] HMF formation from glucose requires a larger amount of $Nb_2O_5 \cdot nH_2O$ than the former. This suggests that the isomerization of glucose into fructose on Lewis acid sites largely participate in the reaction mechanism. There is no difference in HMF formation between $Nb_2O_5 \cdot nH_2O$ and $Na^+/Nb_2O_5 \cdot nH_2O$ without Brønsted acid sites, indicating that HMF formation on $Nb_2O_5 \cdot nH_2O$ does not proceed on the Brønsted acid sites but Lewis acid sites. The tested zeolites with Brønsted and Lewis acid sites did not form HMF. Because zeolite cannot incorporate glucose into micropores (~0.6 nm), less conversion in the case of zeolites is due to reaction only on the external surfaces. It should be noted that the mass balance is not satisfied on $Nb_2O_5 \cdot nH_2O$. This can be attributed to the formation of polymerized species as shown in Figure S6 (SI). Complex side reactions, including aldol condensation among reducing saccharides with formyl groups (−CHO) in the presence of acid catalysts, result in the formation of complex polymers as unknown species that cannot be detected by HPLC and GC−MS.[10] Table 2 also shows that H_3PO_4-treated $Nb_2O_5 \cdot nH_2O$ ($H_3PO_4/Nb_2O_5 \cdot nH_2O$) results in a large decrease in the undetectable products and an increased HMF yield. The catalytic performance remained unchanged even after several catalyst reuses (Figure S7, SI). ^{31}P MAS NMR spectroscopy (Figure S8, SI) and ICP-AES analysis revealed that 1.0 mmol of phosphate ions are tightly fixed on 1 g of $H_3PO_4/Nb_2O_5 \cdot nH_2O$ and ca. 70% (0.10 mmol g^{-1}) of the Brønsted acid sites are covered with phosphate ions. Considering that the Lewis acid sites are not covered with phosphate ions, as shown in Table 2, and the Brønsted acid sites do not play an important role for the reaction, it is expected that most of the phosphate ions (0.90 mmol g^{-1}) are fixed on neutral OH groups on $Nb_2O_5 \cdot nH_2O$, which may reduce undesirable side reactions.

In summary, niobic acid $Nb_2O_5 \cdot nH_2O$ functions as a heterogeneous catalyst with water-tolerant Lewis acid sites for the allylation of benzaldehyde with tetraallyl tin and the conversion of glucose into 5-(hydroxymethyl)furfural (HMF) in water. The Lewis acid sites workable in water are due to NbO_4 tetrahedra that still have effective positive charges as Lewis acid sites even after the formation of NbO_4−H_2O adducts.

ASSOCIATED CONTENT

Supporting Information. Experimental section and Figures S1−S9. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

mhara@msl.titech.ac.jp

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