Chem. Mater. **2005,** *17,* 2487−2489

Exfoliated HNb_3O_8 Nanosheets as a Strong Protonic Solid Acid

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Received November 16, 2004
Revised Manuscript Received April 6, 2005

More than 15 million tons of sulfuric acid is consumed annually as a catalyst in the production of industrially important chemicals. As the cost and inefficiency of separating sulfuric acid from homogeneous reaction mixtures prohibits recycling of sulfuric acid as a catalyst, these processes produce large amounts of acid waste. This situation, coupled with the waste of energy associated with using unrecyclable catalysts, has led to a demand for environmentally benign chemical processes that reduce the impact on the environment and simultaneously increase profits[1−5] through the use of recyclable nontoxic solid acids as replacements for "toxic liquid" acid catalysts.[6−9]

Solid acids should have high stability and strong Brønsted acid sites that function even in the presence of water because water is involved in many industrially important acid-catalyzed reactions.[8] Niobic acid ($Nb_2O_5 \cdot nH_2O$) is a promising candidate for such applications, as it is sufficiently stable and remains active for acid catalysis in the presence of water. $Nb_2O_5 \cdot nH_2O$ is already used for the production of industrially important chemicals such as methyl *tert*-butyl ether, methyl methacrylate, and 2,5-dimethyl-2,4-hexadiene.[10,11] However, the properties of $Nb_2O_5 \cdot nH_2O$ have yet to be examined thoroughly, and although it has been reported that $Nb_2O_5 \cdot nH_2O$ hosts several types of acid sites,[12−17] the details have yet to be clarified, presenting an obstacle to further development of active $Nb_2O_5 \cdot nH_2O$ catalysts. This lack of investigation can largely be attributed to the complexity of amorphous $Nb_2O_5 \cdot nH_2O$.[15−19]

In this study, HNb_3O_8 exfoliated sheets, as two-dimensional (2D) single-crystal metal-oxide sheets obtained from layered HNb_3O_8, were studied as a solid acid catalyst. Layered HNb_3O_8 is a cation-exchangeable layered metal oxide in which H^+ ions are emplaced between 2D $Nb_3O_8^-$ anion nanosheets composed of NbO_6 octahedra.[20] The 2D single-crystal nanosheets have the advantage of permitting a more elegant interpretation of the surface structure and surface functional groups.

HNb_3O_8 exfoliated sheets were prepared by exfoliation and aggregation of layered HNb_3O_8 through soft-solution processing.[20,21] Figures 1c and 1d show the transmission electron microscopy (TEM) image and electron diffraction pattern of colloidal $Nb_3O_8^-$ sheets obtained by the exfoliation processes. The sharp electron diffraction pattern indicates that the $[Nb_3O_8]^-$ sheets retained the original single-crystal sheet structure. Scanning electron microscopy (SEM) images of layered HNb_3O_8 and HNb_3O_8 exfoliated sheets are also shown in Figure 1. The surface area of the layered HNb_3O_8 was only 1 $m^2\ g^{-1}$, while that of HNb_3O_8 exfoliated sheets reached 101 $m^2\ g^{-1}$.

The acid catalytic activity of HNb_3O_8 exfoliated sheets has been demonstrated through the formation and hydrolysis of ethyl acetate.[22] The surface areas and acid catalytic

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(21) Layered HNb_3O_8 was prepared according to the method in the literature.[20] Exfoliated $Nb_3O_8^-$ sheets were obtained by adding 15 wt % tetra(*n*-butylammonium)hydroxide (TBA^+OH^-) solution to 150 mL of distilled water containing 2.0 g of the protonated compounds. TBA^+OH^- solution was added to the suspension until the pH reached 9.0−10.0, and the resultant solution was shaken for 3 days. The insertion of voluminous and hydrophilic TBA^+ cations expands and hydrates the interlayer spaces, resulting in exfoliation. The suspension was then centrifuged, and the supernatant solution containing the nanosheets was collected. The addition of a nitric acid aqueous solution (0.1 M, 20 mL) to 30 mL of the nanosheet solution resulted in immediate random aggregation of the nanosheets as a precipitate. The aggregated sample was then rinsed several times with 100 mL of distilled water to remove HNO_3.

(22) Esterification of acetic acid and hydrolysis of ethyl acetate were carried out in an ethanol−acetic acid mixture (ethanol: 1.0 mol, acetic acid: 0.1 mol) and distilled water containing ethyl acetate (H_2O: 1.7 mol, ethyl acetate: 15 mmol), respectively, in an Ar atmosphere for 6 h. Tested catalysts were evacuated at 453 K for 1 h prior to reaction, and 0.2 and 0.8 g of each catalyst were used in esterification and hydrolysis, respectively. The liquid phase was analyzed during reaction by gas chromatography with capillary columns.

10.1021/cm047990y CCC: $30.25

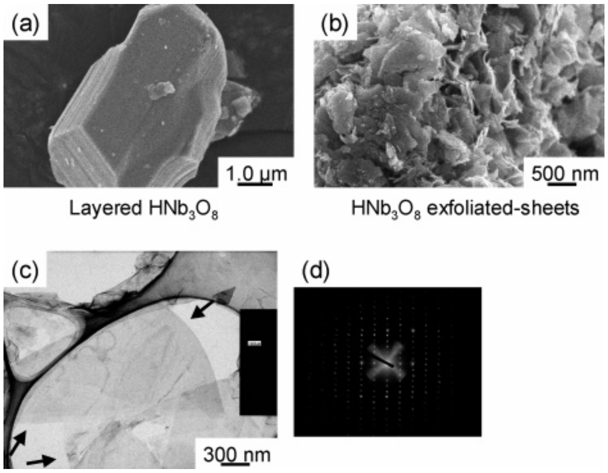

Figure 1. SEM images of (a) layered HNb_3O_8 and (b) aggregated HNb_3O_8 sheets, and (c) TEM image and (d) electron diffraction pattern of colloidal exfoliated $[Nb_3O_8]^-$.

Table 1. Esterification of Acetic Acid and Hydrolysis of Ethyl Acetate by Exfoliated Sheets

catalyst	BET surface area ($m^2\ g^{-1}$)	esterification[a] rate of produced ethyl acetate (μmol min^{-1})	hydrolysis[b] rate of produced ethanol (μmol min^{-1})
HNb_3O_8 exfoliated sheets	101	118	2.33
$Nb_2O_5{\cdot}nH_2O$	128	64	1.07
$SiO_2-Al_2O_3$	685	20	0
$HSr_2Nb_3O_{10}$ exfoliated sheets	65	20	0
layered HNb_3O_8	1	20	0
no catalyst		20	0

[a] Using 0.2 g of catalyst. [b] Using 0.8 g of catalyst.

performances of tested samples are compared in Table 1. As references, the results for $HSr_2Nb_3O_{10}$ exfoliated sheets,[23] $Nb_2O_5{\cdot}nH_2O$ (CBMM Co.) and $SiO_2-Al_2O_3$ (JRC-SAH-1, Si/Al = 2.1) are also shown. $Nb_2O_5{\cdot}nH_2O$ and $SiO_2-Al_2O_3$ are typical commercial solid acid catalysts, while $HSr_2Nb_3O_{10}$ exfoliated sheets are randomly aggregated 2D single-crystal sheets prepared by exfoliation and aggregation of cation-exchangeable layered perovskite $HSr_2Nb_3O_{10}$.[23] $SiO_2-Al_2O_3$, $HSr_2Nb_3O_{10}$ exfoliated sheets, and layered HNb_3O_8 did not catalyze either reaction. In layered HNb_3O_8 molecules are unable to penetrate the narrow interlayer space to utilize interlayer H^+ ions as a catalyst. However, the HNb_3O_8 exfoliated sheets exhibited remarkable catalytic performance for both reactions, reaching twice that of the commercial $Nb_2O_5{\cdot}nH_2O$ catalyst. After the reactions for 6 h, HNb_3O_8 exfoliated sheets were simply recovered by decantation and recycled for further reaction. It was confirmed that the activities for the reactions remained unchanged even after the sample was recycled for a third time. ICP analysis could not detect any leaching metal cations in the solutions after reactions. This indicates that the exfoliated sheets function as a stable and recyclable solid acid catalyst.

To further understand the acid properties, the catalytic activities of the samples in dehydration of 2-propanol[23] and Friedel−Crafts alkylation of anisole[24] were examined. It was confirmed that in dehydration of 2-propanol (atmospheric flow reaction system, catalyst: 0.2 g, 523 K)[23] each sample shows catalytic activity in proportion to that for ethyl acetate formation, and 2-propanol conversion on HNb_3O_8 exfoliated sheets was estimated to be about 90% which was larger than that of $Nb_2O_5{\cdot}nH_2O$ (61%). In Friedel−Crafts alkylation of anisole, HNb_3O_8 exfoliated sheets also exhibited higher catalytic activity (yield: 95.6%, selectivity of phenyl anisole: 98.2%) than $Nb_2O_5{\cdot}nH_2O$ (yield: 28.0%, selectivity of phenyl anisole: 70.3%). These results indicate that HNb_3O_8 exfoliated sheets have a larger number of active acid sites than $Nb_2O_5{\cdot}nH_2O$.

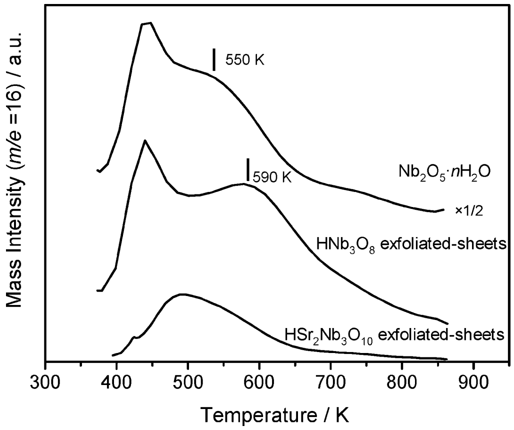

Figure 2. NH_3 TPD (m/e = 16) spectra for $Nb_2O_5{\cdot}nH_2O$, HNb_3O_8 exfoliated sheets, and $HSr_2Nb_3O_{10}$ exfoliated sheets.

Figure 2 shows the NH_3 TPD (m/e = 16) results for $Nb_2O_5{\cdot}nH_2O$, HNb_3O_8 exfoliated sheets, and $HSr_2Nb_3O_{10}$ exfoliated sheets.[25] A large desorption peak for $Nb_2O_5{\cdot}nH_2O$ appears at 450 K with a shoulder at 550 K. As the weak Brønsted acid sites on $Nb_2O_5{\cdot}nH_2O$ are removed at 500 K,[12,14] the desorption shoulder at 550 K can be attributed to strong Brønsted acid sites. The NH_3 TPD profile for HNb_3O_8 exfoliated sheets is composed of two clear peaks, at 450 and 590 K, the higher of which is higher than the temperature of the shoulder peak of $Nb_2O_5{\cdot}nH_2O$, suggesting that HNb_3O_8 exfoliated sheets have stronger acid sites than $Nb_2O_5{\cdot}nH_2O$. In contrast, the NH_3 TPD curve for $HSr_2Nb_3O_{10}$ exfoliated sheets exhibits no desorption peaks above 500 K, indicating that the exfoliated sheets have no strong acid sites.[23]

Although $Nb_2O_5{\cdot}nH_2O$, HNb_3O_8 exfoliated sheets, and $HSr_2Nb_3O_{10}$ exfoliated sheets are all Nb^{5+}-containing oxides, there appears to be a definitive distinction in catalysis and acidity among these materials, suggesting that the appearance of strong Brønsted acid sites is largely structure-dependent. Figure 3 shows ^1H magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra for the $HSr_2Nb_3O_{10}$ exfoliated sheets, HNb_3O_8 exfoliated sheets, and $Nb_2O_5{\cdot}nH_2O$ along with the schematic structures of the sheets.[26]

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(24) Friedel−Crafts alkylation of anisole was carried out in an anisole (100 mmol)−benzyl alcohol (10 mmol) mixture at 423 K. 0.2 g of each catalyst was used in the reaction, and the liquid phase after reaction for 4 h was analyzed by gas chromatography.

(25) The acidity of the samples was tested by NH_3 temperature programmed desorption (TPD). NH_3 TPD was carried out using a TPD-1-AT instrument (BEL Japan) equipped with a quadrupole mass spectrometer. After the sample was heated at 453 K for 1 h under He flow, 20 mg of the sample was exposed to NH_3 at 373 K for adsorption and then heated at 10 K min^{-1}.

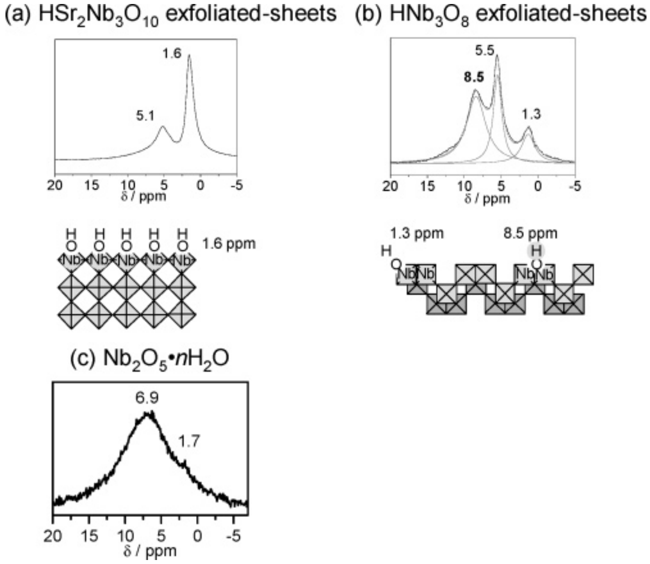

Figure 3. ^{1}H MAS NMR spectra for (a) $HSr_2Nb_3O_{10}$ exfoliated sheets, (b) HNb_3O_8 exfoliated sheets, and (c) $Nb_2O_5\cdot nH_2O$ after dehydration.

On $HSr_2Nb_3O_{10}$ sheets consisting of corner-shared NbO_6 octahedra, H is located only on oxygen atoms at the vertexes of the NbO_6 octahedra. The two peaks at 5.1 and 1.6 ppm in the NMR spectrum for the $HSr_2Nb_3O_{10}$ exfoliated sheets can be assigned to Nb−OH groups with and without hydrogen bonds, respectively.[23] In the NMR spectrum for HNb_3O_8 exfoliated sheets, three peaks appear at 1.3, 5.5, and 8.5 ppm. As the HNb_3O_8 sheets are composed of edge-shared NbO_6 octahedra, it is expected that there are OH groups shared by two Nb^{5+} (Nb(OH)Nb) in addition to isolated Nb−OH groups. As a result, the chemical shift at 8.5 ppm can be attributed to Nb(OH)Nb. This peak has a large chemical shift and is not observed in the ^{1}H MAS NMR spectrum of $HSr_2Nb_3O_{10}$ exfoliated sheets (not an acid catalyst), suggesting that Nb(OH)Nb functions as strong Brønsted acid sites. Figure 3c shows the ^{1}H MAS NMR spectrum for dehydrated $Nb_2O_5\cdot nH_2O$, revealing a broad peak centered around 6.9 ppm with a shoulder at 1.7 ppm. $Nb_2O_5\cdot nH_2O$ is formed by the random condensation of $H_8Nb_6O_{19}$ clusters,[16,18] resulting in a large variety of hydroxyl groups and hence the broad peak in the ^{1}H MAS NMR spectrum. The above NMR spectra show that HNb_3O_8 exfoliated sheets has a high density of surface hydroxyl groups at greater than ca. 8 ppm compared with $Nb_2O_5\cdot nH_2O$, indicating that the HNb_3O_8 exfoliated sheets catalyst has a higher density of strong Brønsted acid sites than $Nb_2O_5\cdot nH_2O$.

In summary, HNb_3O_8 exfoliated sheets obtained from layered HNb_3O_8 were found to function as a strong Brønsted acid catalyst, exceeding the activity of $Nb_2O_5\cdot nH_2O$ in the presence of water. The catalytic performance of HNb_3O_8 exfoliated sheets was attributed to the formation of bridging hydroxyl groups, Nb(OH)Nb, suggesting that Nb(OH)Nb functions as strong Brønsted acid sites also in $Nb_2O_5\cdot nH_2O$. A more detailed study is therefore necessary to determine how the effective acid sites in HNb_3O_8 exfoliated sheets differ from those in $Nb_2O_5\cdot nH_2O$.

Acknowledgment. This work was supported by the Solution Oriented Research for Science and Technology (SORST) program of the Japan Science and Technology Corporation (JST), the 21st Century Center of Excellent (COE) program of the Ministry of Education, Science, Sports and Culture of Japan, and a Grant-in-Aid for Scientific Research (15360427) from the Japan Society for the Promotion of Science (JSPS).

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(26) ^{1}H MAS NMR spectra were measured with a MSL400 spectrometer (Bruker) at a Larmor frequency of 400.13 MHz. A Bruker MAS probehead was used with a 4-mm rotor. The spinning rate of the sample was 8.0 kHz. The ordinary single-pulse sequence was used. The dehydrated samples were packed into the rotor under an N_2 atmosphere. The chemical shifts were expressed with respect to neat tetramethylsilane.