Titanium Niobate and Titanium Tantalate Nanosheets as Strong Solid Acid Catalysts

Atsushi Takagaki,[†] Takemi Yoshida,[†] Darling Lu,[‡] Junko N. Kondo,[†] Michikazu Hara,[†] Kazunari Domen,*,[†,‡] and Shigenobu Hayashi[§]

*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta,
Midori-ku, Yokohama 226-8503, Japan, Core Research for Evolutional Science and Technology (CREST),
Japan Science and Technology Company, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan, and Institute
for Materials & Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST),
Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

$HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets obtained by exfoliation of protonated cation-exchangeable layered metal oxides are examined as solid acids. These nanosheets exhibit high catalytic activity for esterification of acetic acid and hydrolysis of ethyl acetate, competing with niobic acid, $Nb_2O_5 \cdot nH_2O$. NH_3 temperature-programmed desorption reveals that the acidity of the nanosheets corresponds to the density of strong acid sites of H−ZSM-5 or niobic acid. [1]H magic-angle-spinning nuclear magnetic resonance spectroscopy suggests that bridging hydroxyl groups (Ti(OH)M (M = Nb^{5+} or Ta^{5+})) on these titanium niobate/tantalate nanosheets function as strong Brønsted acid sites that are available for this reaction.

Introduction

Homogeneous acid catalysts such as sulfuric acid and HCl, in the liquid phase with reactants and products, are essential in many industrially important reactions but are not environmentally benign and present many operational problems such as neutralization, costly and inefficient catalyst separation from the products, and disposal of the acid catalysts waste as waste. The principles of "green chemistry" and "green technology" dictate that production should have minimal adverse effects on the environment and human health,[1,2] stimulating the replacement of these acid catalysts with recyclable, nontoxic solid acids with strong acid sites.[3]

H^+-exchanged forms of cation-exchangeable transition-metal layered oxides are potentially strong solid acids: H^+ ions are placed between two-dimensional (2D) transition-metal oxide anion sheets. The interlayer H^+ ions, however, cannot react with reactants because the intercalation of reactant molecules is inhibited due to the high charge density of the sheets. Exfoliation of the layered sheets may be an alternative way to overcome this disadvantage, leading to the application of such layered materials in catalytic reactions. Progress in soft-solution processing achieved over the past decade has now made such an attempt possible.

Recently, the authors found that exfoliation of $HTiNbO_5$, a cation-exchangeable layered metal oxide, in an aqueous solution affords colloidal single-crystal $TiNbO_5^-$ sheets, which precipitate under acidic conditions to form aggregates of $HTiNbO_5$ nanosheets. These nanosheet aggregates function as a strong solid acid for some acid-catalyzed reactions such as esterification of acetic acid, cracking of cumene, and dehydration of 2-propanol.[4] In contrast, $HSr_2Nb_3O_{10}$ nanosheets, which can be prepared from layered $HSr_2Nb_3O_{10}$, a layered perovskite com-

pound, exhibited no or only slight activity for acid catalysis in these reactions. Color indicator reagents, NH_3 temperature-programmed desorption (NH_3-TPD), and[1]H magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy revealed that the strong acidity of $HTiNbO_5$ nanosheets, corresponding to 90% sulfuric acid or stronger, is due to bridging hydroxyl groups (Ti(OH)Nb) as a novel type of strong Brønsted acid site.[4] On the other hand, $HSr_2Nb_3O_{10}$ nanosheets containing isolated Nb−OH groups and hydrogen-bonded Nb−OH groups do not exhibit strong acidity, suggesting that exfoliation−aggregation of protonated layered compounds does not always result in strong solid acids and that strong acid sites such as $Ti^{4+}(OH)Nb^{5+}$ are essential for the preparation of nanosheets with strong acidity.

There is a wide variety of cation-exchangeable layered metal oxides, and it is expected that nanosheets capable of forming bridged OH groups (i.e., $Ti^{4+}(OH)Nb^{5+}$) will function as strong solid acids. In this study, several nanosheets ($TiNbO_5^-$, $Ti_2NbO_7^-$, and $TiTaO_5^-$) were prepared by exfoliation of the corresponding H^+-exchanged layered oxides ($HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$). The nanosheet aggregates formed by subsequent precipitation under acidic conditions were examined as potential solid acid catalysts. The schematic structures of these protonated layered oxides are shown in Figure 1. In $HTiNbO_5$, $HTiTaO_5$, and HTi_2NbO_7, H^+ ions are placed between 2D anion sheets composed of TiO_6 and NbO_6 or TaO_6 octahedra.

Experimental Section

Preparation of Polyanion Nanosheets. $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ powders (3−30 μm) were prepared from $KTiNbO_5$, $CsTi_2NbO_7$, and $KTiTaO_5$ powders according to the procedure described in the literature.[5−7] $TiNbO_5^-$ and $Ti_2NbO_7^-$ nanosheets were obtained by adding 15 wt % tetra(*n*-buthyl-ammonium)hydroxide (TBA$^+$OH$^-$) solution to 150 mL of distilled water containing 2.0 g of these protonated compounds.[4,8] TBA$^+$OH$^-$ solution was added to the suspension until the pH reached 9.5−10.0, and the resultant solution was shaken

* To whom correspondence should be addressed. E-mail: kdomen@res.titech.ac.jp.
† Chemical Resources Laboratory, Tokyo Institute of Technology.
‡ CREST, JST.
§ National Institute of Advanced Industrial Science and Technology.

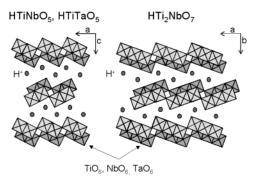**Figure 1.** Schematic structures of several layered metal oxides ($HTiNbO_5$, $HTiTaO_5$ and HTi_2NbO_7).

for 3−7 days. The insertion of voluminous and hydrophilic TBA^+ cations expands and hydrates the interlayer spaces, resulting in the exfoliation of individual metal oxide sheets. The suspension was then centrifuged, and the supernatant solution containing the nanosheets was collected. As the addition of TBA^+OH^- solution did not result in the exfoliation of layered $HTiTaO_5$, a colloidal solution containing $TiTaO_5^-$ nanosheets was obtained by adding 45.2 mmol of ethylamine to 150 mL of distilled water containing 2.0 g of layered $HTiTaO_5$.

The addition of an HNO_3 aqueous solution (1.0 M, 20 mL) to 30 mL of the nanosheet solution resulted in immediate aggregation of the nanosheets as a precipitate. The aggregated samples, $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets, were rinsed 5−10 times with 100 mL of distilled water to remove HNO_3. The complete removal of HNO_3 was confirmed by elemental analysis.

Acid-Catalysis Reactions. Esterification of acetic acid and hydrolysis of ethyl acetate were employed as test reactions to examine the acid properties of the prepared samples. Esterification of acetic acid was performed in the liquid phase as follows: 0.20 g of the catalyst was evacuated at 453 K for 1 h and then added to a mixture of acetic acid (0.10 mol) and ethanol (0.10 mol). In the case of hydrolysis of ethyl acetate, 0.80 g of the sample dehydrated by evacuation was added to 30 mL of an aqueous solution containing 15.3 mmol of ethyl acetate. The reaction was carried out at 343 K in an Ar atmosphere, and the liquid phase was analyzed by gas chromatography with capillary columns.

For comparison, reactions using protonated zeolites (H-MOR, SiO_2/Al_2O_3 = 18.3, JRC-Z-HM20; BET surface area, 205 m^2 g^{-1}), H-ZSM-5 (SiO_2/Al_2O_3 = 90, JRC-Z-5-90H; BET surface area, 421 m^2 g^{-1})), and niobic acid ($Nb_2O_5 \cdot nH_2O$, CBMM Co. Ltd.; BET surface area, 128 m^2 g^{-1}) were also examined.

Characterization. The samples were characterized by X-ray diffraction (XRD; Rint 2000, Rigaku), scanning electron microscopy (SEM; S-4700, Hitachi), and transmission electron microscopy (TEM; 2010F, JEOL).

The acidity of each sample was examined by NH_3-TPD using a TPD-1-AT (BEL Japan) instrument equipped with a quadrupole mass spectrometer. After heating 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}.

^1H MAS NMR spectra were measured at room temperature using a Bruker MSL400 spectrometer at a Larmor frequency of 400.13 MHz. A Bruker MAS probe head was used, coupled with a 4 mm zirconia rotor. The spinning rate of the sample was 8 kHz, and the ordinary single-pulse sequence was used. The frequency of the spectra was expressed with respect to neat tetramethylsilane. Experimentally, adamantane was used as a second reference material, the signal of which was set at 1.87
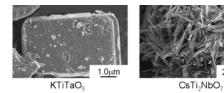

KTiTaO₅   CsTi₂NbO₇

Figure 2. SEM images of layered $KTiTaO_5$ and $CsTi_2NbO_7$.

ppm for spinning at 8 kHz. NMR spectra of dehydrated samples were measured before and after CD_3CN adsorption as follows: Dehydrated samples were obtained in a Pyrex cell in a similar manner as above and exposed to CD_3CN vapor at room temperature for 30 min, followed by evacuation for 1 h at room temperature. The dehydrated and CD_3CN-adsorbed samples were packed into a rotor in a glovebox under an N_2 atmosphere. The seal on the rotor was good, and rehydration of the sample was not observed during NMR measurements.

Results and Discussion

Structures of Nanosheets and Aggregated Nanosheets. SEM images of layered $KTiTaO_5$ and $CsTi_2NbO_7$ are shown in Figure 2. The $KTiNbO_5$ and $KTiTaO_5$ samples were composed of tabular particles of up to 20 μm in size,[4] while $CsTi_2NbO_7$ was made up of rodlike particles. No changes in morphology due to protonation were observed.

Figure 3 shows TEM images and electron diffraction patterns of $TiNbO_5^-$, $Ti_2NbO_7^-$, and $TiTaO_5^-$ nanosheets in colloidal solutions after exfoliation. The sharp electron diffraction patterns indicate that these nanosheets maintain the original crystal structures of the $TiNbO_5^-$ and $Ti_2NbO_7^-$ nanosheets. In contrast to the titanium niobate nanosheets, $TiTaO_5^-$ nanosheets display diffuse or ring-like electron diffraction patterns, indicating that each of the observed $TiTaO_5^-$ nanosheet are not single crystal. Figure 3c(ii) shows that the $TiTaO_5^-$ nanosheets are covered with small particles (2−10 nm), which would result in the observed diffuse or ring-like electron diffraction patterns. Therefore, there appears to be a definitive distinction between the exfoliation behavior of TBA^+OH^- and ethylamine.

The SEM images of the aggregated $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets are shown in Figure 4. The addition of H^+ to solutions containing colloidal nanosheets causes the nanosheets to aggregate randomly as precipitates with the expected compositions (the Ti/M (M = Nb or Ta) ratios for $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets are 0.97, 1.30, and 0.93, respectively), as confirmed by energy-dispersive X-ray spectroscopy, and the resultant is free of the tabular particles observed in the original layered compounds.[4] The Brunauer−Emmett−Teller (BET) surface areas of nanosheets are summarized in Table 1. The surface area of the aggregated $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets is much higher than that of the original protonated layered oxides (about 1 m^2 g^{-1}), indicating that the exfoliation−aggregation processing provides access to the surface of the nanosheets.

Figure 5 shows the XRD patterns of the original and aggregated samples ($HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$). For these nanosheets, the XRD patterns displayed much weaker (00*l*) ($HTiNbO_5$ and $HTiTaO_5$) and (0*k*0) (HTi_2NbO_7) diffraction peaks compared to those of the original layered compounds, while the in-plane diffraction peaks such as (410), (200), and (210) persisted even after exfoliation−aggregation. This indicates that these aggregated nanosheet samples have a poorly periodic layer structure compared to the original layered compounds. This lack of long-range ordering of the layer structure has also been observed for $HSr_2Nb_3O_{10}$ nanosheets.[4]
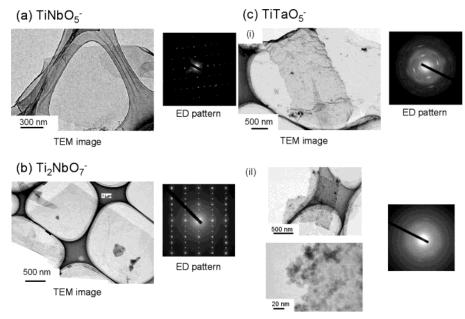
Figure 3. TEM images and electron diffraction patterns of colloidal $TiNbO_5^-$, $Ti_2NbO_7^-$ and $TiTaO_5^-$.
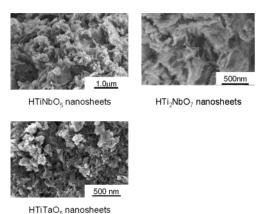

Figure 4. SEM images of aggregated $HTiNbO_5$, HTi_2NbO_7 and $HTiTaO_5$ nanosheets.

TABLE 1: BET Surface Areas of Several Polyanion Nanosheets

Polyanion nanosheets	BET surface area/$m^2\ g^{-1}$
$HTiNbO_5$ nanosheets	153
HTi_2NbO_7 nanosheets	141
$HTiTaO_5$ nanosheets	92

Acid-Catalysis Reactions over Several Polyanion Nanosheets. Figure 6 shows the amount of ethyl acetate formed by esterification of acetic acid for 6 h in the presence of the prepared nanosheets. For comparison, the results for protonated zeolite (H-MOR and H−ZSM-5) and niobic acid ($Nb_2O_5 \cdot nH_2O$) are also shown. Niobic acid is a rare inorganic solid acid that shows acidity in the presence of water. [3,10] These zeolites were evacuated at 773 K for 1 h to remove adsorbed water prior to reaction. As demonstrated in a blank test (no catalyst), ethyl acetate is formed from a mixture of acetic acid and ethanol in the absence of an acid catalyst through acid catalysis of the acetic acid itself.[9] The estimated amount of ethyl acetate produced under equilibrium conditions is 66 mmol, indicating that the equilibrium conditions do not suppress ethyl acetate formation. It has been confirmed previously that layered $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ did not catalyze these reactions.[4] The titanium niobate/tantalate nanosheets ($HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$) exhibited higher acid catalytic activity
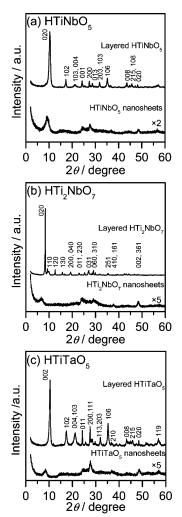

Figure 5. XRD patterns for layered and aggregated samples ($HTiNbO_5$, HTi_2NbO_7 and $HTiTaO_5$).

for the esterification than the protonated zeolites, rivaling $Nb_2O_5 \cdot nH_2O$ catalyst. In tested nanosheets, the rate of ethyl acetate formation decreased with reaction time: the ethyl acetate formation rate after 6 h was about one-half that in the early stage of reaction. After 6 h, these nanosheets were simply
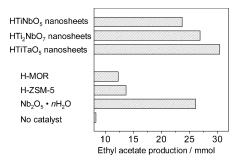
Figure 6. Production of ethyl acetate on each sample at 343 K (catalyst: 0.2 g, acetic acid: 0.10 mol, ethanol: 0.10 mol, reaction time: 6 h).
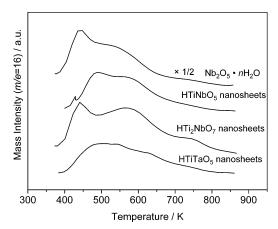

Figure 7. NH_3-TPD ($m/e = 16$) spectra for each aggregated nanosheet (sample: 20 mg).
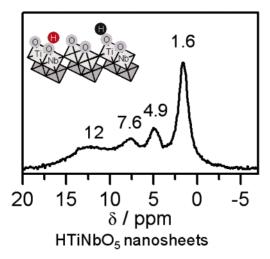
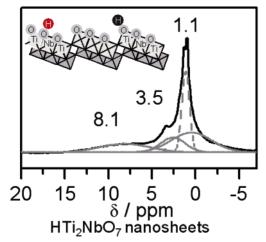**TABLE 2: Hydrolysis of Ethyl Acetate by Exfoliated Nanosheets**

Catalyst	Rate of produced ethanol/μmol g^{-1} min^{-1}
$HTiNbO_5$ nanosheets	1.15
HTi_2NbO_7 nanosheets	1.90
$HTiTaO_5$ nanosheets	2.53
H-MOR	0
$Nb_2O_5 \cdot nH_2O$	1.34
No catalyst	0

recovered by decantation and recycled for further reaction. It was confirmed that time courses of ethyl acetate formation were unchanged even after the samples were recycled for a third time.

The results of hydrolysis of ethyl acetate are summarized in Table 2. H-MOR did not show acid catalysis for the reaction, while $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets also function as active solid acid catalysts even in the presence of excess water. In this reaction, the catalytic activity of $HTiTaO_5$ nanosheets reached about twice that of $Nb_2O_5 \cdot nH_2O$. In the case of hydrolysis by these nanosheets, the rates of ethanol formation were unchanged during reaction.

NH_3-TPD. $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets function as strong solid acid catalysts for esterification reactions. NH_3-TPD was employed to evaluate the acid strengths of these nanosheets. Figure 7 shows the NH_3-TPD ($m/e = 16$) results for prepared nanosheets and $Nb_2O_5 \cdot nH_2O$. $Nb_2O_5 \cdot nH_2O$ produced a large peak at 440 K and another at about 550 K. As the weak Brønsted acid sites on $Nb_2O_5 \cdot nH_2O$ disappear above 500 K,[10] the latter desorption peak is assigned to strong Brønsted acid sites. It is noted that an additional weak peak, which is not completely separated, is observable at ca. 700 K, tailing to above 800 K. $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets exhibited three desorption peaks (ca. 440, 570, and 750 K),
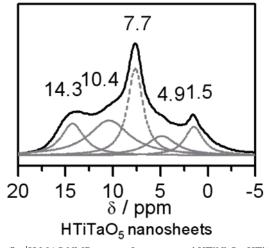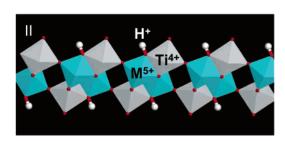

Figure 8. ^{1}H MAS NMR spectra for aggregated $HTiNbO_5$, HTi_2NbO_7 and $HTiTaO_5$ nanosheets at room temperature after removal of adsorbed water.
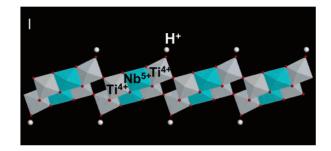
similar to $Nb_2O_5 \cdot nH_2O$. The top temperatures of the second desorption peaks of these niobate/tantalate nanosheets were higher than that for $Nb_2O_5 \cdot nH_2O$ ($HTiNbO_5 = 570$ K, HTi_2-$NbO_7 = 570$ K, $HTiTaO_5 = 640$ K), although the peak intensities were about 40−60% of that for $Nb_2O_5 \cdot nH_2O$. Thus, these nanosheets appear to have lower densities of strong acid sites, but the acid sites are stronger than on $Nb_2O_5 \cdot nH_2O$.

^{1}H MAS NMR for $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ Nanosheets. The properties of hydrogen species on the nanosheets were examined in detail by ^{1}H MAS NMR spectroscopy. The

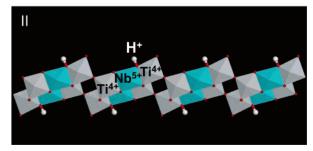Titanium Niobate and Titanium Tantalate Nanosheets

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(A) HTiMO$_5$

(B) HTi$_2$NbO$_7$

Figure 9. Schematic structure of HTiMO$_5$ (M = Nb or Ta) and HTi$_2$NbO$_7$ nanosheets (A: HTiMO$_5$, B: HTi$_2$NbO$_7$).

[1]H chemical shift reflects the acidic property, and hydrogen species with a large chemical shift are expected to possess strong acidity.

The ^{1}H MAS NMR spectra of HTiNbO$_5$, HTi$_2$NbO$_7$, and HTiTaO$_5$ nanosheets after removal of adsorbed water are shown in Figure 8. In the spectra before dehydration, a single peak appears at 6.4−6.7 ppm. The peak of OH groups on the nanosheets merges with the peak for water due to chemical exchange. As it was confirmed by thermogravimetric differential thermal analysis (TG-DTA) that adsorbed water on these nanosheets desorbs at ca. 400 K, the dehydrated samples were obtained by heating at 453 K for 1 h.[4] In the spectrum of aggregated HTiNbO$_5$ nanosheets, four peaks are observed at 1.6, 4.9, 7.6, and 12 ppm. The first three peaks are assigned to isolated Ti−OH, hydrogen-bonded Ti−OH, and Ti(OH)Nb, respectively.[4] Ti(OH)Nb is therefore regarded as a novel strong Brønsted acid corresponding to 90% sulfuric acid or stronger. The peak at 12 ppm is ascribed to OH groups in a similar environment to layered HTiNbO$_5$, suggesting that some of the exfoliated sheets aggregate in a regular stacking pattern. Layered HTiNbO$_5$ exhibits no activity for acid-catalysis reactions, indicating that the OH groups are not available for these reactions in this case.[4]

HTi$_2$NbO$_7$ and HTiTaO$_5$ nanosheets also produced a number of peaks in the NMR spectra. It is essential in the assignment of these peaks to take account of the detailed structures of [TiNbO$_5$]$^-$, [Ti$_2$NbO$_7$]$^-$, and [TiTaO$_5$]$^-$ sheets. Figure 9 shows the schematic structures of HTiNbO$_5$, HTi$_2$NbO$_7$, and HTiTaO$_5$ nanosheets. In [TiNbO$_5$]$^-$ and [TiTaO$_5$]$^-$ sheets there are two kinds of alternating arrangements of TiO$_6$ and MO$_6$ (M = Nb^{5+} or Ta^{5+}) octahedra, and all sheets are expected to consist of both of these arrangements. As it expected that negative charge will be localized on the TiO$_6$ octahedra of sheets obtained by exfoliation of layered compounds, oxygen atoms bonded to only Ti^{4+} on the sheet surface combine with H$^+$ to form isolated Ti−OH in the case of the arrangements in Figure 9A-I (HTiNbO$_5$ and HTiTaO$_5$). When TiO$_6$ and MO$_6$ (M = Nb^{5+} or Ta^{5+}) octahedra are oriented as shown in Figure 9A-II, oxygen atoms shared by Ti^{4+} and M^{5+} bind to H$^+$, resulting in the formation of Ti(OH)M.

HTi$_2$NbO$_7$ nanosheets consist predominantly of two kinds of alternating arrangements, as illustrated in Figure 9B-I and 9B-II. Taking account of the localization of negative charge on the nanosheets after exfoliation, it is expected that isolated Ti−OH and Ti(OH)Nb will be present on HTi$_2$NbO$_7$ nanosheets in addition to HTiNbO$_5$. This indicates that the structures of hydrogen species on these nanosheets are essentially similar. As a result, by analogy with isolated Ti−OH and hydrogen-bonded Ti−OH in HTiNbO$_5$ nanosheets, the chemical shifts at 1.1−1.5 and 3.5−4.9 ppm in HTi$_2$NbO$_7$ and HTiTaO$_5$ nanosheets can be assigned to isolated Ti−OH and hydrogen-bonded Ti−OH, respectively. The NMR spectra of HTi$_2$NbO$_7$ and HTiTaO$_5$ nanosheets also exhibited a broad peak above 7 ppm (peak top = 8.1 ppm) and an intense peak at 7.7 ppm, respectively. These chemical shifts are consistent with that of Ti(OH)Nb on HTiNbO$_5$ nanosheets,[4] and it therefore seems reasonable to assign these peaks at 7−8 ppm to Ti(OH)M (M = Nb^{5+} or Ta^{5+}). It should be noted that in the NMR spectrum for HTiTaO$_5$ nanosheets, two peaks appear at 10.4 and 14.3 ppm. The chemical shift of strongly acidic OH groups fixed in the interlayer space of layered HTiTaO$_5$ appears at ca. 14 ppm, indicating that the peak at 14.3 ppm observed for the nanosheets is attributable to OH groups in a similar environment of layered HTiNbO$_5$. On the other hand, the peak at 10.4 ppm is not observed in the ^{1}H MAS NMR spectra of HTiNbO$_5$ and HTi$_2$NbO$_7$ nanosheets. One possible explanation for this peak is hydrogen-bonded Ti(OH)Ta. Such a chemical shift might not be observed in HTiNbO$_5$ and HTi$_2$NbO$_7$ nanosheets because broad peaks due to the layered structure (>10 ppm) overlap the small peaks of hydrogen-bonded Ti(OH)Nb. Thus, ^{1}H MAS NMR spectra of these nanosheets are basically composed of isolated Ti−OH and Ti(OH)M (M = Nb^{5+} or Ta^{5+}). Aggregation forms hydrogen-bonded species due to these surface OH groups, suggesting that a difference in aggregation of three kinds of nanosheets results in very different NMR spectra.
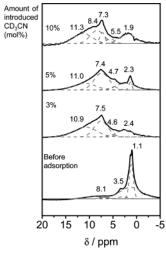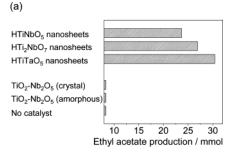
Figure 10. ^{1}H MAS NMR spectra for aggregated HTi$_2$NbO$_7$ nanosheets before and after CD$_3$CN adsorption.

The acid strength of Ti(OH)Nb on HTi$_2$NbO$_7$ nanosheets was evaluated using CD$_3$CN as a probe molecule.[11] It has been reported that the 7.6 ppm peak due to Ti(OH)Nb on HTiNbO$_5$ nanosheets shifts to 11 ppm upon adsorption of CD$_3$CN.[4] This means that the chemical shift in CD$_3$CN-adsorbed HTiNbO$_5$ nanosheets is comparable to that of CD$_3$CN-adsorbed strong Brønsted acid sites in zeolites[11] and that Ti(OH)Nb presumably functions as strong Brønsted acid sites on HTiNbO$_5$ nanosheets. Figure 10 shows the NMR spectra for HTi$_2$NbO$_7$ nanosheets before and after CD$_3$CN adsorption. The adsorption of a small amount of CD$_3$CN on the nanosheets resulted in a dramatic change in the NMR spectrum, with the appearance of strong peaks at ca. 7.5 and 11 ppm and a weakening of the 1.1 ppm peak. Judging from the intensity of each peak before and after CD$_3$CN adsorption, the peaks at 3.5 and 8.1 ppm appear to shift to ca. 7.5 and 11 ppm, respectively, upon CD$_3$CN adsorption. In the case of HTiTaO$_5$ nanosheets, CD$_3$CN adsorption also resulted in a slight shift, whereas the peaks were shifted clearly by H$_2$O adsorption. One possible explanation for the relatively minor change induced by CD$_3$CN adsorption on HTiTaO$_5$ nanosheets is the H-bonding of CD$_3$CN (e.g., CD$_3$C$^+$ = N$-$H) responsible for the strong acidity. Ti(OH)M (M = Nb^{5+} or Ta^{5+}) is regarded as a novel strong Brønsted acid site in these niobate/tantalate nanosheets. By ^{1}H MAS NMR analysis and thermogravimetric analysis (TGA),[12] the densities of strong acid sites (Ti(OH)M) on HTiNbO$_5$, HTi$_2$NbO$_7$, and HTiTaO$_5$ nanosheets have been estimated to be 0.39, 0.36, and 0.37 mmol g^{-1}. These nanosheets show very different NMR spectra but give similar catalytic performance, and this might be explained by the similar effective acid site densities. While there is no remarkable difference in effective acid density and catalytic activity among the nanosheets, HTiTaO$_5$ has the highest catalytic activity: the acidity of Ti(OH)Ta is stronger than that of Ti(OH)Nb. It has been reported that hydrated tantalum oxide (Ta$_2$O$_5 \cdot n$H$_2$O) has stronger Brønsted acid sites than hydrated niobium oxide (Nb$_2$O$_5 \cdot n$H$_2$O), although effective acidic sites are in a similar chemical environment in both oxides.[13] This indicates that OH groups on Ta^{5+} are more acidic than those on Nb^{5+}, suggesting that the strong acidity of Ti(OH)Ta can be attributed to Ta^{5+}. More detailed study is necessary to determine how the electron distribution in Ti(OH)Ta differs from that of Ti(OH)Nb.

It should be noted that Ti^{4+}(OH)M^{5+} strong acid sites appear only on nanosheets prepared from layered compounds. Figure 11A shows the amount of ethyl acetate formed by esterification of acetic acid for 6 h in the presence of two kinds of metal
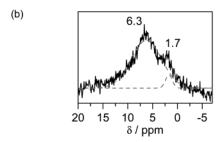

Figure 11. (a) Production of ethyl acetate on titanium niobate/tantalate nanosheets and Ti$-$Nb mixed oxides (343 K, catalyst: 0.2 g, acetic acid: 0.10 mol, ethanol: 0.10 mol, reaction time: 6 h). (b) ^{1}H MAS NMR spectra for Ti$-$Nb mixed oxide composed of TiO$_2$(rutile), Nb$_2$O$_5$ and TiNb$_2$O$_7$ after dehydration.

oxides containing Ti^{4+} and Nb^{5+} (Ti^{4+}:Nb^{5+} = 1:1) (an amorphous oxide and a mixture of crystalline TiO$_2$(rutile), Nb$_2$O$_5$, and TiNb$_2$O$_7$).[13] Neither sample exhibited catalytic activity for the reaction. The ^{1}H MAS NMR spectrum of the mixture of TiO$_2$(rutile), Nb$_2$O$_5$, and TiNb$_2$O$_7$ is shown in Figure 11B (after removal of adsorbed water). Weak peaks are apparent at 1.7 and 6.3 ppm, but there is no peak that can be assigned to Ti(OH)Nb in the spectrum. It was confirmed that the peak due to Ti(OH)Nb was not observed in the ^{1}H MAS NMR spectrum for the amorphous sample. It therefore appears that Ti(OH)Nb cannot be formed on bulky metal oxides prepared simply by mixing Ti^{4+} and Nb^{5+}, suggesting that nanosheets of TiO$_6$ and NbO$_6$ octahedra mixed at an atomic level are essential for the generation of such strong acid sites.

Conclusion

HTiNbO$_5$, HTi$_2$NbO$_7$, and HTiTaO$_5$ nanosheets were shown to function as strong solid acids for the esterification of acetic acid and hydrolysis of ethyl acetate, acid-catalyzed reactions. ^{1}H MAS NMR revealed that the acid catalytic activity of these nanosheets is attributable to strong Brønsted acid sites, presumably Ti(OH)M (M = Nb^{5+} or Ta^{5+}). Such strong acid sites only form on nanosheets prepared by exfoliation$-$aggregation of the protonated-layered transition-metal oxides.

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(12) The density of effective acid sites on $HTiNbO_5$, HTi_2NbO_7, and $HTiTaO_5$ nanosheets was estimated by ^{1}H MAS NMR and TGA. Assuming that the 7.6−8.1 ppm peaks due to Ti(OH)M (M = Nb^{5+} or Ta^{5+}) are attributable to effective strong acid sites for the esterification of acetic acid, the proportion of Ti(OH)M among the total hydroxyl group content was obtained from the ^{1}H MAS NMR spectra for these nanosheets after removal of adsorbed water. The total hydroxyl group content of the nanosheets was estimated by TGA after removal of adsorbed water.

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(14) Two kinds of metal oxides containing Ti^{4+} and Nb^{5+} were prepared by a sol−gel method. $Ti(O^iPr)_4$ and $NbCl_5$ (Ti:Nb = 1:1) were dissolved in an ethanol solution, to which KOH solution was added to induce precipitation. After aging 1 day, the obtained samples were rinsed with HNO_3 and water to remove K^+ and Cl^- ions. The prepared precursors were then heated at 523 or 1073 K for 3 h in air. XRD and energy-dispersive X-ray spectroscopy revealed that both oxide samples consisted of Ti and Nb (Ti:Nb = 1:1) and that the oxides prepared at 523 and 1073 K were an amorphous oxide and a mixture of crystalline TiO_2, Nb_2O_5, and $TiNb_2O_7$, respectively, with particle sizes of ca. 20 and 50 nm. The surface areas of the former and latter were estimated to be 217 and 43 m^2 g^{-1}, respectively.