

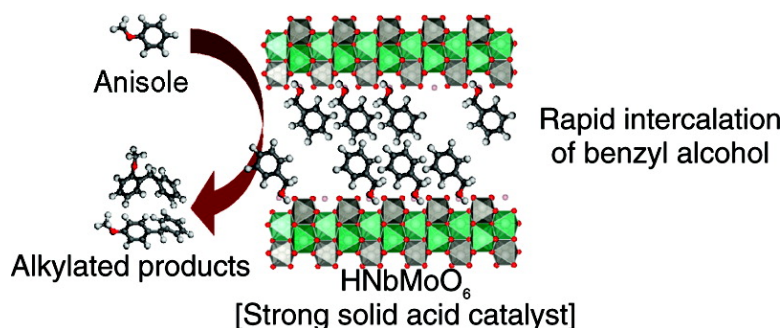
Communication

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## Efficient Utilization of Nanospace of Layered Transition Metal Oxide HNbMoO<sub>6</sub> as a Strong, Water-Tolerant Solid Acid Catalyst

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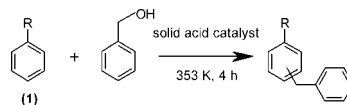
There are inherent drawbacks to the use of liquid acids as catalysts, such as the cost of separating the acid from the reaction solution and the generation of large amounts of waste. Solid acid catalysts, which are reusable and readily separable from the reaction product, offer the opportunity to reduce the impact on the environment and increase profits.<sup>1–4</sup> For this reason, a number of solid acids such as clay minerals,<sup>5</sup> zeolites,<sup>6</sup> Cs-heteropoly acids,<sup>7</sup> sulfated zirconia,<sup>8</sup> ion-exchange resins,<sup>9</sup> and sulfonated-carbon materials<sup>10</sup> have been investigated. Among them, the use of a layered material is one of the fascinating approaches to developing a solid acid catalyst with enhanced activity. Cation-exchangeable clay minerals such as montmorillonite exhibit catalytic activity for acid-catalyzed reactions due to the good contact between interlayer acid sites and the reactants.<sup>5</sup>

Like clay minerals, H<sup>+</sup>-exchanged layered transition-metal oxides are promising materials for use as a solid acid catalyst due to the generation of strong acidity within the interlayer space. However, without modification, the reactants are generally inhibited from penetrating into the interlayer region of layered transition-metal oxides owing to the high charge density of the oxide sheets. One approach to resolving this problem is to exfoliate the layered metal oxide into metal oxide “nanosheets”.<sup>11</sup> Most of the nanosheet materials possess high surface area (ca. 100 m<sup>2</sup>·g<sup>-1</sup>) and exhibit strong catalytic activity for acid-catalyzed reactions such as esterification and hydrolysis, higher than that of zeolites and niobic acid.<sup>11</sup> Nevertheless, this method has a drawback that the acidity of exfoliated nanosheets became weaker than that of the original layered metal oxide.

In this study, the layered transition-metal oxide, HNbMoO<sub>6</sub>·nH<sub>2</sub>O, is demonstrated to exhibit remarkable acid catalysis without exfoliation. This is the first report of successful acid catalysis using a layered transition-metal oxide. Layered HNbMoO<sub>6</sub>·nH<sub>2</sub>O can be obtained easily from the Li form by a proton-exchange reaction. The resultant material consists of layers formed of randomly sited MO<sub>6</sub> (M = Nb and Mo) octahedral with H<sub>2</sub>O in the interlayer.<sup>12</sup>

The acid catalytic activity of layered HNbMoO<sub>6</sub> is demonstrated here through the Friedel–Crafts alkylation, acetalization, esterification, hydrolysis, and hydration. Table 1 lists the catalytic performance results for the Friedel–Crafts alkylation of anisole, toluene, or benzene with benzyl alcohol in liquid phase over layered HNbMoO<sub>6</sub>. For comparison, the results for niobic acid (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O), zeolites and ion-exchange resins are also shown. As we have reported, other layered transition-metal oxides such as HNb<sub>3</sub>O<sub>8</sub> and HTiNbO<sub>5</sub> did not exhibit the activity (Supporting Information, Table S1). However, HNbMoO<sub>6</sub> exhibits remarkable activity for these reactions, much higher than that of other tested

**Table 1.** Friedel–Crafts Alkylation over Some Solid Acid Catalysts<sup>a</sup>



catalyst	acid amount (mmol g <sup>-1</sup> )	yield of alkylate (%) <sup>b</sup>		
		R = OCH <sub>3</sub> <sup>c</sup>	R = CH <sub>3</sub>	R = H
HNbMoO <sub>6</sub> <sup>d</sup>	1.9 <sup>e</sup>	99.0 <sup>f</sup> (89)	74.1 (4.9)	21.9 (1.4)
HNbMoO <sub>6</sub> <sup>g</sup>	1.9 <sup>e</sup>	94.0 <sup>f</sup> (86)	22.2 (1.5)	7.7 (0.5)
Nb <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O	0.3	1.2 (2)	N.D.	N.D.
Nafion NR50	0.9	42.3 (23)	19.0 (2.8)	9.7 (1.4)
Amberlyst-15	4.8	42.1 (5)	14.0 (0.4)	6.7 (0.2)
H-ZSM <sup>5h</sup>	0.2	8.6 (22)	0.9 (0.6)	N.D.
H-Beta <sup>i</sup>	1.0	30.6 (16)	0.6 (0.1)	N.D.

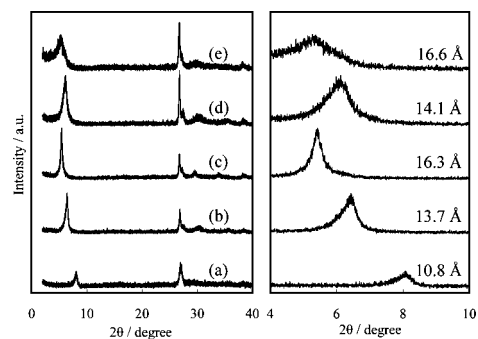
<sup>a</sup> Reaction conditions: **1** (100 mmol), benzyl alcohol (10 mmol), catalyst (0.2 g), 353 K, 4 h. <sup>b</sup> Values in parentheses are turnover rate (h<sup>-1</sup>). N.D. - not determined. <sup>c</sup> Reaction temperature, 373 K; reaction time, 1 h. <sup>d</sup> Protonated with H<sub>3</sub>PO<sub>4</sub>. <sup>e</sup> Determined by <sup>31</sup>P NMR using trimethylphosphine oxide. <sup>f</sup> Reaction time, 30 min. <sup>g</sup> Protonated with HNO<sub>3</sub>. <sup>h</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90, JRC-Z-5-90H. <sup>i</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25, JRC-Z-HB25.

solid acids; the yield of benzyl anisole reached to 99% after 30 min, whereas those for ion-exchange resins reached to ca. 42% even after 1 h. The turnover rate of HNbMoO<sub>6</sub> for the alkylation of anisole was more than three times higher than that of Nafion NR50. HNbMoO<sub>6</sub> also catalyzes the alkylation of toluene or benzene, achieving high yields.

During the alkylation, benzyl alcohol was rapidly consumed in the initial stage of the reaction, while the product formed gradually. This result implies that benzyl alcohol is rapidly intercalated into the layered HNbMoO<sub>6</sub>, where it reacts with anisole, toluene, and benzene to form the product. For confirmation of this process, the adsorption of benzyl alcohol onto HNbMoO<sub>6</sub> was investigated in isolation by immersing HNbMoO<sub>6</sub>·nH<sub>2</sub>O (n = 1.23) in benzyl alcohol solution under constant shaking for 30 min. Figure 1c shows the XRD pattern of the resultant material after drying at room temperature. Immersion in benzyl alcohol shifts the (001) peak due to HNbMoO<sub>6</sub> to lower angles, corresponding to an increase in basal spacing from 13.7 to 16.3 Å. This shift confirms the intercalation of benzyl alcohol into the layered HNbMoO<sub>6</sub>. Given the interlayer spacing of the fully dehydrated sample (10.8 Å),<sup>12</sup> the total expansion is estimated to be 5.5 Å. Although similar experiments were conducted for anisole, toluene, and benzene, no intercalation was indicated. The necessity of intercalated benzyl alcohol for this reaction was further investigated by adding an intercalated sample to anisole solution followed by heating at 373 K for 1 h. Alkylated products were detected after the reaction, and the basal spacing of HNbMoO<sub>6</sub> was found to decrease to 14.1 Å (Figure 1d). Benzyl

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**Figure 1.** XRD patterns of HNbMoO<sub>6</sub>: (a) dehydrated, (b) hydrated ( $n = 1.23$ ), (c) after immersion in benzyl alcohol for 30 min, (d) after reaction of anisole, (e) during Friedel–Crafts alkylation.

**Table 2.** Esterifications of Acetic Acid and Lactic Acid and Hydration of 2,3-Dimethyl-2-butene Catalyzed by HNbMoO<sub>6</sub>

catalyst	esterification of acetic acid, <sup>a</sup> reaction rate (mmol h <sup>-1</sup> )	esterification of lactic acid, reaction rate (mmol h <sup>-1</sup> )	hydration, <sup>b</sup> yield (%)
HNbMoO <sub>6</sub>	2.2 (3)	5.7 (11)	3.4, 3.4 <sup>c</sup>
Nafion NR50	16.0 (84)	6.0 (25)	2.2
Amberlyst-15	13.7 (13)	4.5 (3)	3.7
blank	0.9	1.4	0.4

<sup>a</sup> Reaction conditions: acetic acid or lactic acid (100 mmol), ethanol (1 mol), catalyst (0.2 g), 343 K. Values in parentheses are turnover rate (h<sup>-1</sup>). <sup>b</sup> Reaction conditions: 2,3-dimethyl-2-butene (12.5 mmol), H<sub>2</sub>O (0.42 mol), catalyst (0.2 g), 343 K, 5 h. <sup>c</sup> Third reuse.

alcohol was not detected in the solution. In the Friedel–Crafts alkylation of toluene in the presence of benzyl alcohol, the interlayer spacing of the layered HNbMoO<sub>6</sub> was found by XRD of the extracted catalyst (30 min after reaction) to increase to 16.6 Å (Figure 1e). These results clearly indicate that intercalated benzyl alcohol is consumed in the reaction and that the interlayer sites of HNbMoO<sub>6</sub> function as active sites.

HNbMoO<sub>6</sub> is also able to intercalate *n*-alkyl alcohols and ketones as shown in Figure S1 and S2. For acetalization of cyclohexanone with methanol HNbMoO<sub>6</sub> exhibited a high activity (Table S2). Table 2 shows esterifications of acetic acid (carboxylic acid) or lactic acid (hydroxycarboxylic acid) with ethanol. Ion-exchange resins catalyzed both esterifications and the production rate of ethyl acetate was ca. 3 times higher than that of ethyl lactate. On the other hand, HNbMoO<sub>6</sub> did not catalyze esterification of acetic acid despite the ability of intercalation of ethanol. However, for the esterification of lactic acid HNbMoO<sub>6</sub> exhibited a high catalytic activity, comparable to ion-exchange resins. The XRD indicated that lactic acid can intercalate into the oxide whereas acetic acid does not (Figure S3). Considering that activation of carboxylic acid by proton is necessary for the reaction, esterification of acetic acid did not occur due to the difficulty of intercalation of acetic acid. However, lactic acid which has an OH group adjacent to the carboxyl group could intercalate into the oxide, resulting in a high catalytic activity for the reaction. Similar results were obtained in hydrolysis of ethyl acetate, ethyl lactate and cyclohexyl acetate (Table S3). For three esters, HNbMoO<sub>6</sub> only catalyzes hydrolysis of ethyl lactate.

Table 2 also lists the results for hydration of 2,3-dimethyl-2-butene over HNbMoO<sub>6</sub>. Even in the presence of water, HNbMoO<sub>6</sub> also functioned as an efficient catalyst. The yield of the corresponding alcohol was higher than that of Nafion NR50 and comparable to that of Amberlyst-15. This alkene was able to be intercalated into the oxide which was determined by XRD (Figure S4), resulting in the high catalytic activity. The HNbMoO<sub>6</sub> was

recoverable by filtration and washing with water and acetone to remove the residue within the interlayer, and the material was confirmed to be reusable with no change in crystal structure or activity after three reuse cycles (Table S1 and Table 2).

The acid property of the HNbMoO<sub>6</sub> was evaluated by NH<sub>3</sub> TPD. The NH<sub>3</sub>-TPD profile for HNbMoO<sub>6</sub> is composed of two peaks, at 601 and 682 K (Figure S5), the higher of which is much higher than the temperature of the peaks of zeolites (582 K for H-ZSM5) and niobic acid. The order of desorption peak of these solid acids is consistent with that of the catalytic activity per acid sites for Friedel–Crafts alkylation. <sup>31</sup>P MAS NMR using trimethylphosphine oxide (TMPO) was also carried out. The <sup>31</sup>P chemical shifts of protonated TMPO tend to move downfield, indicating that the resonance peaks with high chemical shifts are due to strong protonic acid. HNbMoO<sub>6</sub> displays distinct peaks at 86.4 and 81 ppm, attributable to strong acid sites (Figure S6). It was also confirmed by XRD that TMPO intercalates in HNbMoO<sub>6</sub> (Figure S7), indicating that the strong acid sites of HNbMoO<sub>6</sub> detectable in the NMR spectrum are present in the interlayer.

HNbMoO<sub>6</sub> intercalates alcohols, ketones, and alkene whereas aromatics and acetic acid do not. The intercalation of protonated layered materials is generally induced by acid–base interaction, indicating that the basicity of substrate and its stability after protonation are main factors to be intercalated or not. A more detailed study is necessary to reveal the intercalation mechanism.

In summary, HNbMoO<sub>6</sub> was found to function as a strong solid acid catalyst, exceeding the activity of zeolites and ion-exchange resins for the Friedel–Crafts alkylation. HNbMoO<sub>6</sub> also exhibited high catalytic activity for acetalization, esterification of hydroxycarboxylic acid, and hydration. The catalytic performance of HNbMoO<sub>6</sub> is attributed to the intercalation of reactants into the interlayer and the development of strong acidity.

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**Supporting Information Available:** Experimental section, Tables S1–S3 and Figures S1–S7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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