Application of group V polyoxometalate as an efficient base catalyst: a case study of decaniobate clusters†

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The base catalytic activity of the decaniobate cluster (TMA)6[Nb10O28]6H2O (TMA+ = tetramethylammonium cation) was studied theoretically and experimentally. Density functional theory calculations showed that the oxygen atoms in the cluster are highly negatively charged and suggested the possibility that the cluster can act as a base catalyst. We demonstrated for the first time that [Nb10O28]6− actually exhibits base catalytic activity for aldol-type condensation reactions including Knoevenagel and Claisen–Schmidt condensation reactions. The catalytic reactions proceeded under ambient conditions, suggesting that [Nb10O28]6− holds promise as a practical strong base catalyst.

1. Introduction

A polyoxometalate (POM), [M2Oy]m−, is an anionic metal-oxide cluster that consists of a given number of [MO6] octahedral units by sharing edges or corners. POMs have been widely used as catalysts, especially for acid-catalyzed, oxidation, and photocatalytic reactions. Recently, Mizuno and coworkers reported that [WO4]3− and [γ-HGeW10O38]7− acted as base catalysts for CO2 fixation and Knoevenagel condensation reaction, respectively. The base catalysis has been ascribed to the negativity of the oxygen atoms, mainly due to the high charge densities of the cluster. These studies have motivated us to develop stronger base catalysts based on POMs.

Our simple working hypothesis is that POM having more electronegative oxygen will exhibit stronger base catalysis. The −n/y value of [M2Oy]m− represents a negative charge averaged over the oxygen atoms without assuming electronic charge transfer from metal to oxygen and thus provides a lower limit of the negativity of the oxygen atom. On the assumption that the −n/y value gives a measure of the basicity of the POMs, group V POMs (M = V, Nb, Ta) are more promising than group VI POM (M = Mo, W) for base catalysts. For example, polyoxoniobates (PONbs) such as hexaniobate ([Nb6O19]12−) and decaniobate ([Nb10O28]6−) cluster have more negative −n/y values (−0.42 and −0.21, respectively) than polyoxotungstates (POWs) such as [HGeW10O38]7−. In this communication, we theoretically compared negative charges of oxygen atoms of [Nb10O28]6− with those of POWs. Then, we applied (TMA)6[Nb10O28]6H2O as homogeneous catalyst for aldol-type condensation reactions such as Knoevenagel and Claisen–Schmidt condensation reactions and revealed for the first time that it acted as a Bronsted base catalyst whose strength is comparable to superbases. This result will open up a new possibility of application of PONbs since their catalytic application has been limited to electrocatalysts and photocatalysts so far.

2. Results and discussion

The structure of [Nb10O28]6− was optimized by density functional theory (DFT) calculations. The structure obtained by optimization (Table S1†) reproduced that determined experimentally by single-crystal X-ray diffraction (XRD) except that bond lengths were elongated by <3% relative to the experimental values. The localized charge of the oxygen atoms obtained by natural bond orbital (NBO) analysis is shown in Fig. 1; this gives a measure of the basicity of the individual oxygen atoms. The NBO charges of the oxygen atoms are much more negative than −0.21, which is the lower limit of the negativity without assuming electronic charge transfer between Nb and O. This result indicates electronic charge transfer from Nb to O...
atoms. Fig. 1 suggests that the four edge-sharing oxygen atoms of \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) are the most active sites for base catalytic reaction.

The electronic charge of the most negative oxygen atom in \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) (−0.873) was compared with those of other typical polyoxometalates such as \([\text{W}_{10}\text{O}_{32}]^{4-}\), \([\text{W}_{6}\text{O}_{19}]^{5-}\), and \([\text{WO}_{4}]^{2-}\) (ref. 5) obtained from the same level of calculation (Fig. 2). The charge of the most negative oxygen atom in \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) (−0.873) was much more negative than those of \([\text{W}_{10}\text{O}_{22}]^{4-}\) (−0.753) and \([\text{W}_{6}\text{O}_{19}]^{5-}\) (−0.721), but was slightly less negative than that of \([\text{WO}_{4}]^{2-}\) (−0.934). This comparison suggests that \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) will show base catalysis as in the case of POWs reported so far.\(^5\)

To test the base catalytic activity of \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) cluster dispersed in organic solvent, we synthesized the TMA salt, \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{MeOH}\) (1 : 1) exhibited a series of mass peaks assigned to \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\) reported previously (Fig. 3). The ESI-MS of the product in water–MeOH (1 : 1) exhibited a series of mass peaks assigned to \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) to an accuracy of <0.5% (calcd: C, 14.94; H, 4.36; N, 4.36; Nb, 48.2). Found: C, 14.75; H, 4.38; N, 4.37; Nb, 48.7). These results show that \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) was successfully synthesized.

We applied \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) as a homogeneous catalyst for the Knoevenagel condensation reaction. This is a fundamental coupling reaction to form carbon–carbon double bonds between active methylene compounds such as nitriles (donors) and carbonyl compounds (acceptors). The key step in the reaction is proton abstraction from donors by base catalysts. We studied whether \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) catalyzed the coupling reaction between benzaldehyde (1) and various nitriles having different pK\(_a\) values. The results of the catalytic reactions are summarized in Table 1. \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) cluster did not show any activity for the reactions (entries 1-1 and 2-1) whose pK\(_a\) values are 12.3 and 16.0 even at mild temperature \(T = 313\) K (entries 1-1 and 2-1). Negative-ion ESI-MS of the catalyst after the reaction (entry 2-1) exhibited a series of mass peaks of \((\text{TMA})_6[\text{H}_{(5-x)}\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) (x = 1–3) (Fig. S1†),\(^8\) suggesting that the catalysts did not decompose. Turnover frequencies for these reactions (entries 1-2 and 2-2) were calculated to be 66 and 28 h\(^{-1}\) at 343 K, respectively, from the kinetic data (Fig. S2†).\(^8\) \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) cluster showed base catalytic activity for nitriles 2c (pK\(_a\) = 19.4, entry 3), 2d (pK\(_a\) = 19.5, entry 4), 2e (pK\(_a\) = 21.9, entry 5) and 2f (pK\(_a\) = 23.8, entry 6), although the yields gradually decreased with an increase in the pK\(_a\) values of the nitriles. However, \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) cluster did not show any activity for the reaction of 2g (pK\(_a\) = 32.5, entry 7).

Catalytic activity of \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]^{6-}\cdot\text{H}_2\text{O}\) for Claisen–Schmidt condensation reaction between 1 and acetophenone (2b, pK\(_a\) = 24.7) was also studied. As shown in Scheme 1, \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) also acted as a homogeneous base catalyst for Claisen–Schmidt condensation.

Although the yields of the reactions with 2f (pK\(_a\) = 23.8) and 2h (pK\(_a\) = 24.7) were lower compared to typical base catalysts such
The best of our knowledge, \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) could activate less acidic nitriles indicated its strong basicity. To comparable to the base strength of a catalyst is high as 24.7 if we assume that the base strength of a catalyst is among various POMs. The base strength of \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) is an example of a strong base catalyst that can activate

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### Table 1 Knoevenagel condensation catalyzed by \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]\cdot 6\text{H}_2\text{O}\)

| Entry | Donor | \(pK_a\) | Temp. (K) | Yield (%) |
|-------|-------|--------|-----------|-----------|
| 1-1   | 2a    | 12.3   | 313       | 61        |
| 1-2   | 2a    | 16.0   | 343       | 88        |
| 2-1   | 2b    | 19.4   | 313       | 77        |
| 2-2   | 2b    | 21.9   | 343       | 88        |
| 3     | 2c    | 23.8   | 343       | 39        |
| 4     | 2d    | 25.7   | 343       | 35        |
| 5     | 2e    | 28.5   | 343       | 0         |
| 6     | 2f    | 32.5   | 343       | 0         |
| 7     | 2g    | 32.5   | 343       | 0         |

\(^a\) Reaction conditions: catalyst (1 mol% with respect to 1), 1 (1.0 mmol), 2 (1.0 mmol), MeOH 1 mL, 343 K, 24 h.

### Scheme 1 Claisen–Schmidt condensation catalyzed by \((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]\cdot 6\text{H}_2\text{O}\)

| Entry | Donor | \(pK_a\) | Temp. (K) | Yield (%) |
|-------|-------|--------|-----------|-----------|
| 1-1   | 2a    | 12.3   | 313       | 61        |
| 1-2   | 2a    | 16.0   | 343       | 88        |
| 2-1   | 2b    | 19.4   | 313       | 77        |
| 2-2   | 2b    | 21.9   | 343       | 88        |
| 3     | 2c    | 23.8   | 343       | 39        |
| 4     | 2d    | 25.7   | 343       | 35        |
| 5     | 2e    | 28.5   | 343       | 0         |
| 6     | 2f    | 32.5   | 343       | 0         |
| 7     | 2g    | 32.5   | 343       | 0         |

\(^a\) Reaction conditions: catalyst (1 mol% with respect to 1), 1 (1.0 mmol), 2 (1.0 mmol), MeOH 1 mL, 343 K, 24 h.

3. Conclusions

We have reported for the first time that decaniobate cluster \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) acts as a strong and homogeneous base catalyst for Knoevenagel condensation reaction of benzaldehyde and p-methoxyphenylacetonitrile (\(pK_a = 23.8\)) and Claisen–Schmidt condensation reaction of benzaldehyde and acetophenone (\(pK_a = 24.7\)). This high catalytic activity is associated with the large negative charge on the oxygen sites (−0.79 to −0.87) originating mainly from the large total negative charge on the cluster.

4. Experiment and theory

4.1. Density functional theory calculations

DFT calculations were conducted using the Gaussian 09 program.\(^{22}\) The structure of \([\text{Nb}_{10}\text{O}_{28}]^{6-}\) was optimized at the level of B3LYP/6-31G++(d). The absence of imaginary frequencies was confirmed from vibrational analysis. Natural bond orbital (NBO) analysis was conducted to obtain localized charge on the oxygen atoms.

4.2. Chemicals

Niobic acid was supplied from CBMM (\(\text{Nb}_2\text{O}_5\cdot 7\text{H}_2\text{O}, \text{water} 20\% \text{w/w})\). Tetramethylammonium hydroxide pentahydrate (TCI, 97%), benzaldehyde (Wako, 98%), 4-nitrobenzyl cyanide (TCI, 98%), 4-cyanophenylacetoneitrile (Aldrich, 97%), 3-bromobenzyl cyanide (Wako, 98%), phenylacetonitrile (Wako, 98%), 4-methoxyphenylacetoneitrile (Aldrich, 97%), propionitrile (Wako, 98%), and acetophenone (Wako, 98.5%) were used without further purification. Deionized water (Milli-Q, >18 MΩ cm) was used in all experiments.

4.3. Synthesis

\((\text{TMA})_6[\text{Nb}_{10}\text{O}_{28}]\cdot 6\text{H}_2\text{O}\) was synthesized according to the literature procedure.\(^{23}\) In an autoclave, niobic acid (\(\text{Nb}_2\text{O}_5\cdot 7\text{H}_2\text{O}, \text{water} 20\% \text{w/w}, 3.00 \text{~g, 9.02 mmol}\)) was mixed with 30 mL of EtOH solution of tetramethylammonium hydroxide (3.60 g, 19.9 mmol). The autoclave was heated at 120 °C for 18 h. After the reaction, the orange solution was removed and a white precipitate was collected by centrifugation. The precipitate was washed with EtOH (150 mL) and acetone (150 mL) and dried well. The crude product was dissolved into 50 mL of MeOH and centrifuged to remove unreacted niobic acid. The solution was concentrated into 15 mL by evaporation and separated into three vials. Recrystallization was conducted by adding 20 mL of acetone slowly to each solution to form a second layer. Typical yield was 2.01 g (1.04 mmol, 58% based on Nb).

4.4. Characterization

The powder XRD pattern was collected with a Rigaku SmartLab 3 using nickel-filtered Cu-Kz radiation. Negative-ion ESI-MS was measured with a JEOL JMS-T100LP AccuTOF LC-plus. \((\text{TMA})_6^{6-}\)
[\text{NB}_{10}\text{O}_{28}]\cdot6\text{H}_2\text{O} \text{ was dissolved into water–MeOH (1:1, 1 mg mL}^{-1}) \text{ and electrosprayed at a bias voltage of −2 kV. The mass spectrum was calibrated by using Cs}_nI_{(n+1)} \text{ clusters generated from CsI solution as a reference. Elemental analysis for C, H, and N was conducted with an Elementar vario MICRO cube. ICP-AES analysis for Nb was performed with a Thermo Scientific iCAP DUO-6300 at a wavelength of 309.4 nm. GC analysis was conducted with a Shimadzu GC-2014 with a Restek Rtx-1 (internal diameter \(0.53 \text{ mm, length } = 30 \text{ m}\) capillary column), and GC-MS analysis was conducted with a Shimadzu GCMS-QP2010 Ultra with a Restek Rtx-1 (internal diameter \(0.32 \text{ mm, length } = 30 \text{ m}\) capillary column at an ionization voltage of 70 eV.)

4.5. Catalytic test

Benzaldehyde (1, 1.0 mmol), nitrile or acetophenone (2, 1.0 mmol), and biphenyl (internal standard, ca. 0.1 mmol) were dissolved into MeOH, and \text{[TMA]}_6[\text{NB}_{10}\text{O}_{28}]\cdot6\text{H}_2\text{O} (10 \mu\text{mol, 1 mol%}) \text{ was added to start the reaction. The reaction mixture was stirred for 24 h and then analysed by GC and GC-MS.}

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