Base catalytic application of polyanionic metal oxide clusters

<u>Seiji Yamazoe,</u>[a,b,c,d,]*** Shun Hayashi,**[a] **Naoto Sasaki,**[a] **Tatsuya Tsukuda**[a,b,]*****
[a] *Department of Chemistry, School of Science, The University of Tokyo, Tokyo, 113-0033, Japan*
[b] *Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615–8520, Japan*
[c] *CREST, Japan Science and Technology Agency, Japan*
[d] *Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, 192-0397, Japan (present affiliation)*
**Corresponding author: +81-42-677-2525, yamazoe@tmu.ac.jp*

Abstract: Polyanionic metal oxide cluster, $[Nb_{10}O_{28}]^{6-}$, was found to act as both Brønsted and Lewis base catalysts for Knoevenagel condensation and CO_2 fixation reactions, respectively, in sharp contrast to acid catalysis of bulk Nb_2O_5. Density functional theory calculation suggested that the group V metal oxide clusters are more basic than the group VI clusters. We demonstrated that the base catalytic activities of $[M_6O_{19}]^{n-}$ (M = Nb, Ta, Mo, W) for Knoevenagel condensation and CO_2 fixation reactions increased with the increase of the negative electronic charge of surface oxygen atoms of the clusters.

Keywords: polyoxometalate, base catalyst, CO_2 fixation.

1. Introduction

Metal oxide clusters, called as polyoxometalates, have been widely used as catalysts and building blocks of functional materials. For example, metal oxide clusters are well known as strong acids, but their application as base catalysts has been limited. Recently, Mizuno *et al*. reported that $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ and $[WO_4]^{2-}$ acted as base catalysts.[1,2] High stability of niobium oxide clusters such as $[Nb_6O_{19}]^{8-}$ and $[Nb_{10}O_{28}]^{6-}$ in basic solutions suggests that they will act as base catalysts.[3] In order to test this hypothesis, the base catalysis of $[Nb_{10}O_{28}]^{6-}$ was studied using Knoevenagel condensation and CO_2 fixation reactions as test reactions. In addition, the electronic charge of surface oxygen atoms of metal oxide clusters was evaluated by density functional theory calculations to reveal the origin of their strong basicity. The correlation between the activity and the negative charge on the surface O sites was confirmed by comparing base catalysis of a series of $[M_6O_{19}]^{n-}$ (M = Nb, Ta, Mo, W).

2. Experimental

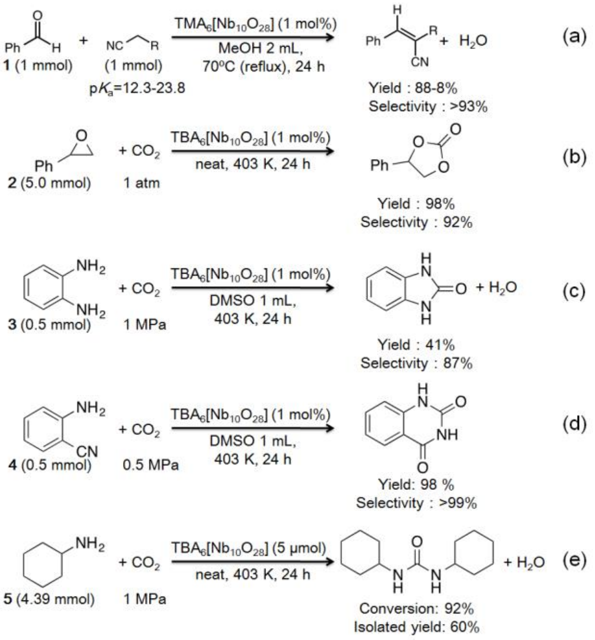
We synthesized $(TMA)_6[Nb_{10}O_{28}]\cdot 6H_2O$ (TMA = tetramethylammonium), $(TBA)_6[Nb_{10}O_{28}]$ (TBA = tetrabutylammonium), $(TBA)_nH_{8-n}[Nb_6O_{19}]$, $(TBA)_2[Mo_6O_{19}]$, $(TBA)_nH_{8-n}[Ta_6O_{19}]$, $(TBA)_2[W_6O_{19}]$ according to the literature with slight modifications.[4–8] The products were characterized by negative-ion electrospray ionization mass spectrometry (ESI-MS), powder X-ray diffraction (PXRD), X-ray absorption spectroscopy (XAS), and elemental analysis.

Electronic charges on the surface O atoms of various metal oxide clusters were estimated theoretically by using Gaussian 09 package. Structural optimization and natural bond orbital (NBO) analysis were conducted by using the B3LYP density functional theory (DFT) method with the basis sets of LanL2DZ and 6-31++G* for M (M = Nb, Mo, Ta, W) and O, respectively.

The metal oxide clusters were applied as homogeneous catalysts for Knoevenagel condensation reaction between benzaldehyde (**1**) and a variety of nitriles having different pK_a values. Brønsted basicity of the clusters was evaluated based on whether or not the reaction was catalyzed via proton abstraction from the nitrile by the catalysts. In addition, these clusters were used as Lewis base catalysts for CO_2 fixation to epoxide and amines, including styrene oxide (**2**), *o*-phenylenediamine (**3**), 2-aminobenzonitrile (**4**), and cyclohexylamine (**5**). Products were identified and quantified by gas chromatography mass spectroscopy and gas chromatography.

3. Results and discussion

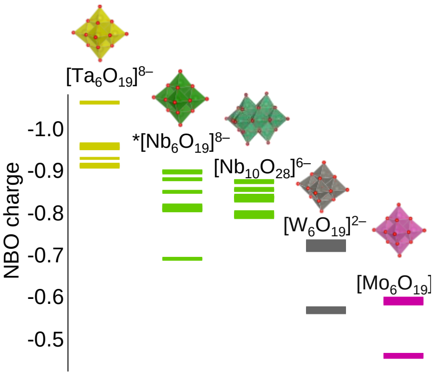
$[Nb_{10}O_{28}]^{6-}$ catalyzed Knoevenagel condensation between **1** and various nitriles whose pK_a values were smaller than 23.8 (Scheme 1a): the yields of the products gradually decreased with an increase in the pK_a values of the nitriles.[4] These results demonstrated that $[Nb_{10}O_{28}]^{6-}$ could be viewed as Brønsted base. $[Nb_{10}O_{28}]^{6-}$ also showed Lewis base catalysis for CO_2 fixation reaction to **2** (Scheme 1b). Theoretical and NMR results indicated that the CO_2 fixation was initiated with the activation of CO_2 on $[Nb_{10}O_{28}]^{6-}$. $[Nb_{10}O_{28}]^{6-}$ was effective for CO_2 fixation reactions to various amines **3**, **4**, **5** (Scheme 1c–e) although high pressure of CO_2 (>0.5 MPa) was necessary to promote the reaction.



Scheme 1. Reaction conditions and catalytic activities for Knoevenagel condensation (a) and CO_2 fixation (b–e) reactions.

Next, the NBO charges of the surface O atoms were calculated to estimate the basicity of the metal oxide clusters (Figure 1). The O atoms of group V metal oxide clusters ($[Nb_6O_{19}]^{8-}$, $[Nb_{10}O_{28}]^{6-}$, $[Ta_6O_{19}]^{8-}$) are charged more negatively than those of group VI metal oxide clusters ($[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$). These results suggest that group V metal oxide clusters, especially $[Ta_6O_{19}]^{8-}$, act as more active base catalysts than group VI clusters.

The above design principle was tested by comparing base catalysis of $[M_6O_{19}]^{n-}$. Group V metal oxide clusters, $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$, showed stronger Brønsted basicity than group VI metal oxide clusters because Knoevenagel condensation reaction between **1** and (4-methoxyphenyl)acetonitrile (pK_a = 23.8) proceeded only by $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$. $[Ta_6O_{19}]^{8-}$ exhibited the strongest Lewis basicity in the CO_2 fixation reaction to **2**.[5]



*Crystal structure

Figure 1. NBO charges of surface oxygen atoms in metal oxide clusters. The thickness represents the number of oxygen with the corresponding NBO charge in the surface.

4. Conclusions

Group V metal oxide clusters ($[Nb_{10}O_{28}]^{6-}$ and $[M_6O_{19}]^{n-}$ (M = Nb, Ta)) were applied to base catalysts. $[Nb_{10}O_{28}]^{6-}$ acted as Brønsted and Lewis base catalysts for Knoevenagel condensation and CO_2 fixation reactions, respectively. DFT calculation showed that surface O atoms of group V metal oxide clusters are charged more negatively than those of group VI clusters, suggesting that group V metal oxide clusters have strong basicity among polyanionic metal oxide clusters. We demonstrated that base catalytic activities of the series of $[M_6O_{19}]^{n-}$ for Knoevenagel condensation and CO_2 fixation reactions increased with an increase in the negative electronic charge of the surface O atoms.

References

1. K. Sugahara, *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 13248.
2. T. Kimura, *et al*. *Angew. Chem., Int. Ed.* **2012**, *51*, 6700.
3. S. Yamazoe *et al*. *Chem. Lett*. **2013**, *42*, 380.
4. S. Hayashi, *et al. RSC Adv.* **2016**, *6*, 16239.
5. S. Hayashi *et al. Chem.Asian J.* **2017**, *12*, 1635.
6. N. H. Hur *et al. Inorg. Synth.* **1990**, *27*, 77.
7. M. Fournier *Inorg. Synth.* **1990**, *27*, 80.
8. M. Matsumoto *et al. Inorg. Chem. Commun.* **2011**, *14*, 115.