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Base Catalysis of Sodium Salts of $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ Mixed-Oxide Clusters

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Abstract: The solid base catalysis of sodium salts of Lindqvist-type metal oxide clusters was investigated using a Knoevenagel condensation reaction. We successfully synthesized the sodium salts of Ta and Nb mixed-oxide clusters $\text{Na}_{8-n}\text{H}_n[(\text{Ta}_{6-x}\text{Nb}_x)\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ ($\text{Na-Ta}_{6-x}\text{Nb}_x$, $n = 0, 1$, $x = 0-6$) and found them to exhibit activity for proton abstraction from nitrile substrates with a pK_a value of 23.8, which is comparable to that of the conventional solid base MgO . The Ta-rich Na-Ta_6 and $\text{Na-Ta}_4\text{Nb}_2$ exhibited high activity among Ta and Nb mixed-oxide clusters. Synchrotron X-ray diffraction (SXRD) measurements, Fourier-transform infrared (FT-IR) spectroscopy, and X-ray absorption spectroscopy (XAS) revealed the structure of $\text{Na-Ta}_{6-x}\text{Nb}_x$: (1) The crystal structure changed from $\text{Na}_7\text{H}[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ to $\text{Na}_8[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ ($\text{M} = \text{Ta}$ or Nb) by the anisotropic expansion of the unit cell with an increase in Ta content; (2) Highly symmetrical Lindqvist $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ was generated in $\text{Na-Ta}_4\text{Nb}_2$ and Na-Ta_6 because of the symmetrical association of Na^+ ions with $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ in the structure. DFT calculation revealed that the Lindqvist structures with high symmetry have large NBO charges on surface oxygen species, which are strongly related to base catalytic activity, whereas the composition hardly affects the NBO charges. The above results showed that the Brønsted base catalysis was sensitive to the symmetry of the Lindqvist $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ structure. These findings contribute to the design of solid base catalysts composed of anionic metal oxide clusters with alkaline-metal cations.

Keywords: solid base catalyst; metal oxide cluster; Lindqvist structure; mixed-oxide metalate

1. Introduction

Metal oxide clusters (MOCs), referred to as polyoxometalates, are well known as super acid catalysts [1–4], photocatalysts [5,6], and redox catalysts [7,8]. Especially, biomass conversion using the acidity and redox property is one of the attractive applications of MOCs [9,10]. Recently, the base catalysis of MOCs attracted substantial attention because negatively charged MOCs proved to have base catalytic properties [11–13]. Mizuno and co-workers reported that monooxometalate $[\text{WO}_4]^{2-}$ [11,12] and defective Keggin-type MOC $[\gamma\text{-H}_2\text{GeW}_{10}\text{O}_{36}]^{6-}$ [13] worked as homogeneous base catalysts. The density functional theory (DFT) revealed that the basicity of MOCs is related to the negative charges of the oxygen atoms within them. Thus, they achieved the strong basicity of MOCs by increasing the negative charge of the clusters with lacunary Keggin-type structures. Our group and Ge et al. found that group V (Nb, Ta) MOCs such as $[\text{Nb}_6\text{O}_{19}]^{8-}$ [14,15],

$[\text{Ta}_6\text{O}_{19}]^{8-}$ [14], $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ [16–19], and $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ [20] showed stronger Brønsted and Lewis base catalysis than group VI (Mo, W) MOCs for Knoevenagel condensation and CO_2 fixation reactions, respectively. Among them, $[\text{Ta}_6\text{O}_{19}]^{8-}$ exhibited the strongest Brønsted base properties being able to abstract protons from nitriles with a $\text{p}K_a$ value of 23.8 in a homogeneous catalytic system because $[\text{Ta}_6\text{O}_{19}]^{8-}$ has negatively charged oxygen atoms, as calculated by DFT [14]. These MOCs also work as base catalysts in solid form. Zhao et al. reported that solid $\text{Na}_8\text{H}[\text{PW}_9\text{O}_{34}]$ salt was active for the Knoevenagel condensation reactions of benzaldehyde with malononitrile ($\text{p}K_a = 11.1$) and ethyl cyanoacetate ($\text{p}K_a = 13.1$) [21]. Similar base strength was obtained for $\text{Na}_{16}[\text{SiNb}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ [20] and $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 13\text{H}_2\text{O}$ salts [15]. However, to date, the base strength of solid MOCs has not been investigated. It could be considered that oxygen atoms with high electron density should be designed to form strong basic sites. Besides, heteroatom doping is one possible way of tuning the electron density of surface oxygen atoms of MOCs [22,23].

Here, we synthesized the sodium salts of Ta–Nb MOCs with a Lindqvist structure $\text{Na}_{8-n}\text{H}[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ ($\text{Na-Ta}_{6-x}\text{Nb}_x$, $n = 0, 1$, $x = 0–6$) and investigated their base strength using a Knoevenagel condensation reaction, which includes the proton abstraction from nitriles with various $\text{p}K_a$ -value C–H bonding [24,25]. We found that the alkali-metal MOC salts showed superior Brønsted base catalytic properties compared with the conventional metal oxide base catalysts. Interestingly, Brønsted basic activity of $\text{Na-Ta}_{6-x}\text{Nb}_x$ was not in the order of negative charge of the oxygen atoms of free $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ clusters, which is one of the significant factors for the base strength [13]. The structural analysis revealed that the symmetry of the MO_6 unit in the Lindqvist $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ was affected by the packing of Na^+ in the crystal and that Na-Ta_6 and $\text{Na-Ta}_4\text{Nb}_2$ had high MO_6 octahedral symmetry among $\text{Na-Ta}_{6-x}\text{Nb}_x$. In addition, we found that the symmetry of the MO_6 unit in the Lindqvist $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ was strongly related to the base catalytic activity. These findings contribute to the design of solid base catalysts composed of anionic metal oxide clusters with alkaline-metal cations.

2. Materials and Methods

The $\text{Na}_{8-n}\text{H}[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ ($\text{Na-Ta}_{6-x}\text{Nb}_x$, $n = 0, 1$, $x = 0, 2, 3, 4$, and 6) were fabricated by the combination of the modified solid-state reaction and the dissolution-precipitation method [26]. The mixture of M_2O_5 ($\text{M} = \text{Ta}$ or Nb), $\text{Na}_2\text{C}_2\text{O}_4$, and $(\text{NH}_2)_2\text{CO}$ at a molar ratio of $(\text{Ta} + \text{Nb})\text{:Na}\text{:}(\text{NH}_2)_2\text{CO}$ of 1:1:4 was calcined at 773 K for 4 h and then 1373 K for 4 h. The obtained powder with a Na_3MO_4 structure was treated with NaOH solution. The resulting white precipitate was centrifuged and washed ($\text{Na-Ta}_{6-x}\text{Nb}_x$). NaTaO_3 and NaNbO_3 were synthesized by a modified solid-state reaction [26] in which the mixture of Ta_2O_5 (or Nb_2O_5), $\text{Na}_2\text{C}_2\text{O}_4$, and $(\text{NH}_2)_2\text{CO}$ at a molar ratio of M ($\text{M} = \text{Ta}$ or Nb): $\text{Na}\text{:}(\text{NH}_2)_2\text{CO}$ of 1:1:4 was calcined at 773 K for 4 h [27]. MgO was supplied from the Catalytic Society of Japan (JRC-MGO-4). The high-resolution synchrotron XRD (SXR) measurements were performed for $\text{Na-Ta}_{6-x}\text{Nb}_x$ using the large Debye–Scherrer camera equipped at beamline BL02B2 in SPring-8. Incident beams were monochromatized to 0.77531 Å. Powder samples were loaded into Pyrex capillaries with an i.d. of 0.2 mm. The sealed capillary was rotated during the measurements to reduce the effect of the preferred orientation of crystallites. The obtained SXR data were analyzed by the RIETAN-FP program [28]. The structure model was displayed using the VESTA program [29]. The structures of MOCs in solid form were investigated using a Fourier-transform infrared spectrometer (JASCO, FT/IR-4600) equipped with an attenuated total reflection accessory (JASCO, ATR PRO ONE). The local structures of $\text{Na-Ta}_{6-x}\text{Nb}_x$ were investigated by Ta L_{3-} and L_{1-} , and Nb K-edges X-ray absorption spectroscopy (XAS) performed at BL01B1 in SPring-8. The spectra were recorded in transmittance mode using ionization chambers at room temperature. Si(111) and Si(311) double-crystal monochromators were used to obtain the incident X-ray beam for Ta L_{3-} and L_{1-} edges X-ray absorption fine structure (XAFS) and Nb-K edge XAFS spectra, respectively. XAFS spectra were analyzed using xTunes software [30]. The k^3 -weighted χ spectra were extracted as the extended X-ray absorption

fine structure (EXAFS) after normalization. The EXAFS spectra in the k range 3.0–17.0 Å^{−1} were Fourier-transformed into r space to obtain FT-EXAFS spectra.

The base catalytic properties of the solid catalysts were investigated using Knoevenagel condensation reaction. Benzaldehyde (1 mmol), nitrile [1 mmol: *a*, ethyl cyanoacetate ($pK_a = 13.1$); *b*, 4-cyanophenylacetonitrile ($pK_a = 16.0$); *c*, (3-chlorophenyl)acetonitrile ($pK_a = 19.5$); *d*, phenylacetonitrile ($pK_a = 21.9$); *e*, (4-methoxyphenyl)acetonitrile ($pK_a = 23.8$)], and biphenyl (internal standard, 0.1 mmol) were dissolved into dimethyl sulfoxide (2 mL). The Knoevenagel condensation reactions were started by the addition of alkali-metal MOC solid catalysts (5 μmol as MOC) into the reaction solution at 303 K or 343 K for 24 h. Metal oxide catalysts (5 mg) were activated by calcination at 473 K or 673 K prior to the reaction.

The DFT calculations and natural bonding orbital (NBO) analysis of the MOCs were performed by using the Gaussian 09 program, in accordance with the literature [14]. The optimized structures of the $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ were calculated by B3LYP incorporating the solvation effect of DMSO using PCM (dielectric constant = 46.826). We employed the LANL2DZ basis sets for Ta and Nb atoms and 6-31++G(d) basis sets for O atom to investigate the effect of the composition of the clusters on the NBO charge of O atoms. To determine the effect of structural distortion on the NBO charge, the NBO analysis was conducted using the crystal structures of Na-Nb₆ and Na-Ta₆ without structural optimization by B3LYP using basis sets of LANL2DZ for Ta and Nb atoms and 6-31++G(d) for O atom.

3. Results and Discussion

Figure 1 shows the catalytic activities of Na-Ta₆ and Na-Nb₆ MOCs for the Knoevenagel condensation reaction (Scheme 1), which enables C–C bond formation via proton abstraction from nitrile by the base catalysts. The stronger base catalysts show activities for this reaction, with nitriles having higher pK_a values. Both Na-Ta₆ and Na-Nb₆ showed catalytic activities for the Knoevenagel condensation reactions with *a* ($pK_a = 13.1$) and *b* ($pK_a = 16.0$) at 303 K. Na-Ta₆ and Na-Nb₆ also exhibited base catalytic activities for *c* ($pK_a = 19.5$), *d* ($pK_a = 21.9$), and *e* ($pK_a = 23.8$) at 343 K, although the activities gradually decreased with increasing pK_a values of nitriles. The activity of Na-Ta₆ for all substrates was higher than that of Na-Nb₆. Figure 2 summarizes the base catalytic activities of Na-Ta_{6-x}Nb_x mixed-oxide MOCs, and common solid base metal oxides in the Knoevenagel condensation reaction with *d* ($pK_a = 21.9$) at 343 K. The activity over Na-Ta_{6-x}Nb_x MOCs was in the order of Na-Ta₆ ≈ Na-Ta₄Nb₂ > Na-Ta₃Nb₃ ≈ Na-Ta₂Nb₄ > Na-Nb₆. The base catalytic activities of Ta₂O₅, Nb₂O₅, and perovskite NaTaO₃ and NaNbO₃ were negligible. Therefore, the cluster structures are important for strong basicity. Among the metal oxide catalysts, activated MgO, treated at 673 K under vacuum conditions for 1 h, showed the base catalytic activity, whereas low activity was obtained over MgO treated at 473 K. This is because MgO has strong base sites of $pK_a \geq 23$ [31], which are passivated by the adsorption of H₂O and CO₂. Therefore, Na-Ta_{6-x}Nb_x salts acted as solid base catalysts without pretreatment, and their strong basicity is comparable to that of activated MgO. Recently, we have reported that the surrounding environment of MOCs is significant for base catalysis because the Brønsted base catalytic activity was suppressed by blocking the base sites on MOCs with counter cations [18]. Next, the structural analysis of Na-Ta_{6-x}Nb_x was performed.

Figure 3A shows the SXRD patterns of Na-Ta_{6-x}Nb_x. All patterns can be indexed on an orthorhombic unit cell with a space group of $Pmnn$, which is consistent with the previous report of Na₈[Ta₆O₁₉]·15H₂O and Na₇H[Nb₆O₁₉]·14H₂O [32]. Here, the Na content in the unit cell is different between Na-Ta₆ and Na-Nb₆ MOCs, but the atomic positions are almost similar despite the additional Na-site in Na-Ta₆ (Figure 4). No impurity phase was detected in all patterns. The lattice parameters obtained by Le Bail analysis are plotted against x in Figure 3B. The compounds show an anisotropic expansion of the lattice, where the a and c axes increase with x while the b axis decrease. The monotonic changes in the lattice suggest the successful formation of a solid solution. However, the lattice parameters

deviate from Vegard's law. In addition, the volume increases in the range of $0 \leq x \leq 4$, whereas the volume decrease in the high x region. These behaviors possibly relate to the change in the Na content during the change in the Ta/Nb content. Since the structure contains two different Ta/Nb sites (Wyckoff positions of 4g and 8g sites), it is interesting to consider the site selectivity of the Ta/Nb positions. Thus, we attempted to carry out Rietveld refinements for the solid solution using $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ structure [32]. However, meaningful selectivity cannot be detected in all compositions.

Figure 1. The conversions of nitriles with various pK_a in Knoevenagel condensation reaction for 24 h over Na-Ta₆ (yellow) and Na-Nb₆ (green). Benzaldehyde, 1 mmol; nitrile substrates *a–e*, 1 mmol; catalyst, 5 μmol ; solvent, DMSO 2 mL; temperature, 303 K for *a* and *b* or 343 K for *c–e*; atmosphere, N₂ 1 atm.

Scheme 1. Knoevenagel condensation reaction of nitrile substrates with benzaldehyde.

Figure 2. Conversions of *d* ($pK_a = 21.9$) in Knoevenagel condensation reaction over Na-Ta_{6-x}Nb_x and reference catalysts. Reaction conditions: benzaldehyde, 1 mmol; *d*, 1 mmol; catalyst, 5 μmol for Na-Ta_{6-x}Nb_x or 5 mg for other metal oxides; solvent, DMSO 2 mL; temperature, 303 K; atmosphere, N₂ 1 atm. MgO was activated at 673 K under vacuum, whereas other metal-oxide catalysts were pretreated at 473 K.

Figure 3. (A) SXRD patterns of Na-Ta_{6-x}Nb_x with the corresponding reference patterns. (a) $x = 0$, (b) 2, (c) 3, (d) 4, and (e) 6. (B) Lattice parameters for Na-Ta_{6-x}Nb_x ($x = 0, 2, 3, 4$, and 6). Right axis represents the unit cell volume.

Figure 4. The Lindqvist-unit structure of (A) Ta₆O₁₉ in Na₈[Ta₆O₁₉]·15H₂O and (B) Nb₆O₁₉ in Na₇H[Nb₆O₁₉]·15H₂O with surrounding Na atoms within 2.6 Å. Color codes: yellow, Ta; green, Nb; red, O; purple, Na; pink, 25%-occupied Na.

The local structure of the Lindqvist M₆O₁₉ unit was investigated using FT-IR and XAS. Figure 5 shows the FT-IR spectra of Na-Ta_{6-x}Nb_x in a region of metal-oxygen stretching patterns. The FT-IR spectrum of Na-Nb₆ showed the characteristic absorption bands of the terminal Nb–O_t and bridging Nb–O_b–Nb vibration of the Lindqvist hexaniobate structure [33,34]. As for Na-Ta₆, since Ta–O_t in Na₈[Ta₆O₁₉]·15H₂O (1.81 Å for Ta1–O4 and Ta2–O2) is longer than Nb–O_t in Na₇H[Nb₆O₁₉]·15H₂O (1.77 Å for Nb1–O4 and 1.79 Å for Nb2–O2), the absorption band of the Ta–O_t vibration in Na-Ta₆ appeared at a lower frequency than that of Nb–O_t in Na-Nb₆. The absorption band of M–O_t (M = Ta and Nb) in Na-Ta₄Nb₂ was also observed at a lower frequency than that of Nb–O_t in Na-Nb₆, whereas those of Na-Ta₂Nb₄ and Na-Ta₃Nb₃ hardly shifted, being consistent with the deviation from Vegard's law in lattice parameters, as shown in Figure 3B. Thus, the surroundings of the Lindqvist unit of Na-Ta₄Nb₂ are similar to those of Na-Ta₆.

Figure 5. (A) FT-IR spectra of Na-Ta_{6-x}Nb_x. (a) $x = 0$, (b) 2, (c) 3, (d) 4, and (e) 6, and (B) corresponding extended view.

X-ray absorption near edge structure (XANES) spectra supported the structural change in the Lindqvist M₆O₁₉ unit of Na-Ta_{6-x}Nb_x with a Ta-rich composition. The pre-edge-peak intensity of XANES spectra of group V, VI, and VII compounds is known as an indicator of the coordination number, d -electron number, and coordination symmetry [35–37]. Figure 6A shows Ta L₁-edge XANES spectra of Na-Ta_{6-x}Nb_x. Compared with Na-Ta₆, Nb-rich Na-Ta_{6-x}Nb_x MOCs exhibited high pre-edge peak intensity, which is attributed to the electronic transition from the $2p$ to $5d$ – $6p$ hybrid orbital formed by the structural distortion from the octahedral (O_h) symmetry of the TaO₆ unit. These results indicate that the O_h symmetry of TaO₆ in the Lindqvist M₆O₁₉ of Na-Ta₄Nb₂ and Na-Ta₆ is higher than that of Na-Ta₃Nb₃ and Na-Ta₂Nb₄. Nb K-edge XANES spectra exhibited a similar decrease in pre-edge-peak intensity (electronic transition from $2p$ to $4d$ – $5p$ hybrid orbital) with a Ta-rich composition (Figure 6B). Thus, Na-Ta₄Nb₂ has a NbO₆ unit with higher O_h symmetry in the Lindqvist structure than Na-Nb₆. Ta L₃- and Nb K-edges extended X-ray absorption fine structure (EXAFS) oscillations of Na-Ta_{6-x}Nb_x robustly indicated the formation of solid solution. (Figure 6C,D). In Ta L₃-edge Fourier-transformed EXAFS of Na-Ta_{6-x}Nb_x (Figure 6E), the two peaks assigned to Ta–Nb and Ta–Ta bonds appeared in Na-Ta₄Nb₂, Na-Ta₃Nb₃, and Na-Ta₂Nb₄, and peak intensity of Ta–Ta increased with increasing Ta content. Similar results were obtained for Nb K-edge FT-EXAFS (Figure 6F) that the Nb–Ta peaks appeared at a long distance, and this intensity gradually increased with an increasing amount of Ta.

The structural analyses revealed that: (1) Na-Ta_{6-x}Nb_x was composed of [Ta_{6-x}Nb_xO₁₉]⁸⁻ mixed-oxide clusters; (2) Na-Ta₆ and Na-Ta₄Nb₂ had Na₈[Ta_{6-x}Nb_xO₁₉]·15H₂O crystal structure whereas others were Na₇H[Ta_{6-x}Nb_xO₁₉]·15H₂O; (3) O_h symmetry of MO₆ in Na-Ta₆ and Na-Ta₄Nb₂ was higher than that in other Na-Ta_{6-x}Nb_x. It was reported that the Brønsted base strength of MOCs depends on the electron density of the surface oxygen atoms [13,14]. The cluster compositions and structural distortion are expected to affect the electronic state of surface O atoms. First, we estimated the NBO charges of surface oxygen atoms of free [Ta_{6-x}Nb_xO₁₉]⁸⁻ clusters by DFT calculations to investigate the effect of cluster composition on the NBO charge. The DFT calculations revealed that the order of the average NBO charge of surface oxygen atoms was [Ta₆O₁₉]⁸⁻ (−1.01) > [Ta₄Nb₂O₁₉]⁸⁻ (−0.98) > [Ta₃Nb₃O₁₉]⁸⁻ (−0.97) > [Ta₂Nb₄O₁₉]⁸⁻ (−0.95) > [Nb₆O₁₉]⁸⁻ (−0.93) as shown in Figure 7A. However, the NBO charge of Ta-coordinated O atoms hardly changed with Nb substitution both for terminal and bridging O atoms. Thus, Brønsted base activity of Na-Ta_{6-x}Nb_x salts could not be explained by the NBO charge of the surface oxygen atoms in the free [Ta_{6-x}Nb_xO₁₉]⁸⁻ clusters.

Figure 6. (A) Ta L_{1-} and (B) Nb K-edge XANES spectra. (C) Ta L_{3-} and (D) Nb K-edge EXAFS oscillations and (E) Ta L_{3-} and (F) Nb K-edge Fourier transforms. (a) Na-Ta₆, (b) Na-Ta₄Nb₂, (c) Na-Ta₃Nb₃, (d) Na-Ta₂Nb₄, (e) Na-Nb₆.

Figure 7. (A) Average NBO charges on O atoms in free $[\text{Ta}_6\text{O}_{19}]^{8-}$, $[\text{Ta}_4\text{Nb}_2\text{O}_{19}]^{8-}$, $[\text{Ta}_3\text{Nb}_3\text{O}_{19}]^{8-}$, $[\text{Ta}_2\text{Nb}_4\text{O}_{19}]^{8-}$, and $[\text{Nb}_6\text{O}_{19}]^{8-}$ clusters. (B) Average NBO charges on O atoms in $[\text{M}_6\text{O}_{19}]^{8-}$ ($\text{M} = \text{Ta}$ or Nb) unit of $\text{Na}_8[\text{Ta}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ and $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$. Color codes: yellow, Ta-coordinated O atoms; green, Nb-coordinated O atoms; red, total O atoms. Terminal and bridging O atoms represent solid and dashed lines, respectively.

Next, we investigated the effect of structural distortion of MO_6 in the clusters on the NBO charge by DFT calculation because XAFS analysis indicated that the O_h symmetry of MO_6 in $\text{Na-Ta}_4\text{Nb}_2$ and Na-Ta_6 was higher than that in other $\text{Na-Ta}_{6-x}\text{Nb}_x$, which is induced by the symmetrical locations of Na ions in the crystal structure. The $[\text{M}_6\text{O}_{19}]^{8-}$ geometries in $\text{Na}_7\text{H}[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ as low O_h MO_6 and $\text{Na}_8[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ as high O_h MO_6 were used in this study ($\text{M} = \text{Ta}$ or Nb). The average NBO charge of surface oxygen atoms of Lindqvist $[\text{M}_6\text{O}_{19}]^{8-}$ in $\text{Na}_8[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ was higher than those in $\text{Na}_7\text{H}[\text{M}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ (Figure 7B). This result showed that the high O_h symmetry of MO_6 in the Lindqvist structure with the symmetrical association of Na^+ ions induces highly negatively charged O atoms. Besides, in the case of low O_h MO_6 , the cationic charge of M atoms decreases due to the interaction between $2p$ orbitals of the O atoms and d orbitals of M atoms. The higher base catalytic activities of $\text{Na-Ta}_4\text{Nb}_2$ and Na-Ta_6 could be explained by the large NBO charges of surface O atoms induced by the high O_h symmetry of MO_6 . The above results showed that the Brønsted base catalysis was sensitive to the symmetry of the MO_6 unit in the Lindqvist $[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}]^{8-}$ structure.

4. Conclusions

Ta and Nb mixed-oxide clusters $\text{Na}_{8-n}\text{H}[\text{Ta}_{6-x}\text{Nb}_x\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ ($\text{Na-Ta}_{6-x}\text{Nb}_x$, $n = 0, 1$, $x = 0-6$) in solid form exhibited activities for proton abstraction from nitrile substrates with a $\text{p}K_a$ value up to 23.8, which is comparable to that of the conventional solid base MgO . The Ta-rich Na-Ta_6 and $\text{Na-Ta}_4\text{Nb}_2$ showed high activities among Ta and Nb mixed-oxide clusters. The structural analysis using SXRD, FT-IR, and XAS revealed that $\text{Na-Ta}_4\text{Nb}_2$ has a similar structure to $\text{Na}_8[\text{Ta}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$, with a highly symmetrical MO_6 in Lindqvist structure ($\text{M} = \text{Ta}$ or Nb) compared with that of Nb_6O_{19} in $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$. On the other hand, $\text{Na-Ta}_3\text{Nb}_3$ and $\text{Na-Ta}_2\text{Nb}_4$ have the same crystal structure to $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$. In a series of $\text{Na-Ta}_{6-x}\text{Nb}_x$ MOCs, the crystal structure had a large impact on the activity. NBO analysis using MO_6 unit of $\text{Na}_8[\text{Ta}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ and $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ revealed that high O_h symmetry of MO_6 in Lindqvist structure induces the negative charges on O atoms. For the design of solid base catalytic sites, it is essential to control the symmetry of the MO_6 unit in the MOC by using cation packing in the crystal structure.

Author Contributions: S.K. and S.Y. designed this study. M.T., K.S. (Kanao Shibata), Y.F. and J.H. synthesized and characterized catalysts and carried out the catalytic tests. K.S. (Kazuki Shibusawa) and N.N. carried out the DFT calculations and analyzed the NBO charges of the catalysts. T.Y. measured and analyzed the SXRD. S.K., M.T. and S.Y. measured and analyzed the XAFS spectra. All authors have read and agreed to the published version of the manuscript.

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References

- Olah, G.A.; Sommer, J.; Namanworth, E. Stable carbonium ions. XLI: Protonated aliphatic alcohols and their cleavage to carbonium ions. *J. Am. Chem. Soc.* **1967**, *89*, 3576–3581. [\[CrossRef\]](#)
- Birchall, T.; Gillespie, R. Nuclear magnetic resonance studies of the protonation of weak bases in fluorosulfuric acid: V. Ketones, carboxylic acids, and some other oxygen bases. *Can. J. Chem.* **1965**, *43*, 1045–1051. [\[CrossRef\]](#)
- Mizuno, N.; Misono, M. Heterogeneous catalysis. *Chem. Rev.* **1998**, *98*, 199–218. [\[CrossRef\]](#)
- Kozhevnikov, I.V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem. Rev.* **1998**, *98*, 171–198. [\[CrossRef\]](#) [\[PubMed\]](#)
- Suzuki, K.; Mizuno, N.; Yamaguchi, K. Polyoxometalate photocatalysis for liquid-phase selective organic functional group transformations. *ACS Catal.* **2018**, *8*, 10809–10825. [\[CrossRef\]](#)
- Iwase, Y.; Tomita, O.; Naito, H.; Higashi, M.; Abe, R. Molybdenum-substituted polyoxometalate as stable shuttle redox mediator for visible light driven Z-scheme water splitting system. *J. Photochem. Photobiol. A Chem.* **2018**, *356*, 347–354. [\[CrossRef\]](#)
- Sadakane, M.; Steckhan, E. Electrochemical properties of polyoxometalates as electrocatalysts. *Chem. Rev.* **1998**, *98*, 219–238. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, S.S.; Yang, G.Y. Recent advances in polyoxometalate-catalyzed reactions. *Chem. Rev.* **2015**, *115*, 4893–4962. [\[CrossRef\]](#) [\[PubMed\]](#)
- Albert, J.; Mehler, J.; Tucher, J.; Kastner, K.; Streb, C. One-step synthesizable Lindqvist–isopolyoxometalates as promising new catalysts for selective conversion of glucose as a model substrate for lignocellulosic biomass to formic acid. *ChemistrySelect* **2016**, *1*, 2889–2894. [\[CrossRef\]](#)
- Cheng, F.; Wang, H.; Rogers, R.D. Oxygen enhances polyoxometalate-based catalytic dissolution and delignification of woody biomass in ionic liquids. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2859–2865. [\[CrossRef\]](#)
- Kimura, T.; Kamata, K.; Mizuno, N. A bifunctional tungstate catalyst for chemical fixation of CO₂ at atmospheric pressure. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 6700–6703. [\[CrossRef\]](#)
- Kimura, T.; Sunaba, H.; Kamata, K.; Mizuno, N. Efficient [WO₄]^{2−}-catalyzed chemical fixation of carbon dioxide with 2-aminobenzonitriles to quinazoline-2,4(1H,3H)-diones. *Inorg. Chem.* **2012**, *51*, 13001–13008. [\[CrossRef\]](#) [\[PubMed\]](#)
- Sugahara, K.; Kimura, T.; Kamata, K.; Yamaguchi, K.; Mizuno, N. A highly negatively charged gamma-Keggin germanodecatungstate efficient for Knoevenagel condensation. *Chem. Commun.* **2012**, *48*, 8422–8424. [\[CrossRef\]](#)
- Hayashi, S.; Sasaki, N.; Yamazoe, S.; Tsukuda, T. Superior base catalysis of group 5 hexametalates [M₆O₁₉]^{8−} (M = Ta, Nb) over group 6 hexametalates [M₆O₁₉]^{2−} (M = Mo, W). *J. Phys. Chem. C* **2018**, *122*, 29398–29404. [\[CrossRef\]](#)
- Xu, Q.; Niu, Y.; Wang, G.; Li, Y.; Zhao, Y.; Singh, V.; Niu, J.; Wang, J. Polyoxoniobates as a superior Lewis base efficiently catalyzed Knoevenagel condensation. *Mol. Catal.* **2018**, *453*, 93–99. [\[CrossRef\]](#)
- Hayashi, S.; Yamazoe, S.; Koyasu, K.; Tsukuda, T. Application of group V polyoxometalate as an efficient base catalyst: A case study of decaniobate clusters. *RSC Adv.* **2016**, *6*, 16239–16242. [\[CrossRef\]](#)
- Hayashi, S.; Yamazoe, S.; Koyasu, K.; Tsukuda, T. Lewis base catalytic properties of [Nb₁₀O₂₈]^{6−} for CO₂ fixation to epoxide: Kinetic and theoretical studies. *Chem. Asian J.* **2017**, *12*, 1635–1640. [\[CrossRef\]](#) [\[PubMed\]](#)
- Hayashi, S.; Yamazoe, S.; Tsukuda, T. Base catalytic activity of [Nb₁₀O₂₈]^{6−}: Effect of counteranions. *J. Phys. Chem. C* **2020**, *124*, 10975–10980. [\[CrossRef\]](#)
- Gutierrez, L.F.; Nope, E.; Rojas, H.A.; Cubillos, J.A.; Sathicq, A.G.; Romanelli, G.P.; Martínez, J.J. New application of decaniobate salt as basic solid in the synthesis of 4H-pyrans by microwave assisted multicomponent reactions. *Res. Chem. Intermed.* **2018**, *44*, 5559–5568. [\[CrossRef\]](#)
- Ge, W.; Wang, X.; Zhang, L.; Du, L.; Zhou, Y.; Wang, J. Fully-occupied Keggin type polyoxometalate as solid base for catalyzing CO₂ cycloaddition and Knoevenagel condensation. *Catal. Sci. Technol.* **2016**, *6*, 460–467. [\[CrossRef\]](#)
- Zhao, S.; Chen, Y.; Song, Y.-F. Tri-lacunary polyoxometalates of Na₈H[PW₉O₃₄] as heterogeneous Lewis base catalysts for Knoevenagel condensation, cyanosilylation and the synthesis of benzoxazole derivatives. *Appl. Catal. A* **2014**, *475*, 140–146. [\[CrossRef\]](#)
- Simms, C.; Kondinski, A.; Parac-Vogt, T.N. Metal-addenda substitution in plenary polyoxometalates and in their modular transition metal analogues. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2559–2572. [\[CrossRef\]](#)

23. Anderson, T.M.; Rodriguez, M.A.; Stewart, T.A.; Bixler, J.N.; Xu, W.; Parise, J.B.; Nyman, M. Controlled assembly of $[\text{Nb}_{6-x}\text{W}_x\text{O}_{19}]^{(8-x)-}$ ($x = 0-4$) Lindqvist ions with (amine)copper Complexes. *Eur. J. Inorg. Chem.* **2008**, *2008*, 3286–3294. [[CrossRef](#)]
24. Isobe, K.; Hoshi, T.; Suzuki, T.; Hagiwara, H. Knoevenagel reaction in water catalyzed by amine supported on silica gel. *Mol. Divers.* **2005**, *9*, 317–320. [[CrossRef](#)] [[PubMed](#)]
25. Tran, U.P.N.; Le, K.K.A.; Phan, N.T.S. Expanding applications of metal–organic frameworks: Zeolite imidazolate framework ZIF-8 as an efficient heterogeneous catalyst for the Knoevenagel reaction. *ACS Catal.* **2011**, *1*, 120–127. [[CrossRef](#)]
26. Yamazoe, S.; Shibata, K.; Kato, K.; Wada, T. Needle-like NaNbO_3 synthesis via $\text{Nb}_6\text{O}_{19}^{8-}$ cluster using Na_3NbO_4 precursor by dissolution–precipitation method. *Chem. Lett.* **2013**, *42*, 380–382. [[CrossRef](#)]
27. Fukada, M.; Shibata, K.; Imai, T.; Yamazoe, S.; Hosokawa, S.; Wada, T. Fabrication of lead-free piezoelectric NaNbO_3 ceramics at low temperature using NaNbO_3 nanoparticles synthesized by solvothermal method. *J. Ceram. Soc. Jpn.* **2013**, *121*, 116–119. [[CrossRef](#)]
28. Izumi, F.; Momma, K. Three-dimensional visualization in powder diffraction. *Solid State Phenom.* **2007**, *130*, 15–20. [[CrossRef](#)]
29. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276. [[CrossRef](#)]
30. Asakura, H.; Yamazoe, S.; Misumi, T.; Fujita, A.; Tsukuda, T.; Tanaka, T. xTunes: A new XAS processing tool for detailed and on-the-fly analysis. *Radiat. Phys. Chem.* **2020**, *175*, 108270–108273. [[CrossRef](#)]
31. Matsuhashi, H.; Nagashima, K.; Naijo, N.; Aritani, H. Surface base sites of MgO covered with Al_2O_3 : XANES analysis of Al and Mg K-edges. *Top. Catal.* **2010**, *53*, 659–663. [[CrossRef](#)]
32. Anderson, T.M.; Rodriguez, M.A.; Bonhomme, F.; Bixler, J.N.; Alam, T.M.; Nyman, M. An aqueous route to $[\text{Ta}_6\text{O}_{19}]^{8-}$ and solid-state studies of isostructural niobium and tantalum oxide complexes. *Dalton Trans.* **2007**, 4517–4522. [[CrossRef](#)]
33. Ma, P.T.; Chen, G.; Wang, G.; Wang, J.P. Cobalt–sandwiched Lindqvist hexaniobate dimer $[\text{Co(III)H}_5(\text{Nb}_6\text{O}_{19})_2]^{8-}$. *Russ. J. Coord. Chem.* **2011**, *37*, 772–775. [[CrossRef](#)]
34. Besserguenev, A.V.; Dickman, M.H.; Pope, M.T. Robust, alkali-stable, triscarbonyl metal derivatives of hexametalate anions, $[\text{M}_6\text{O}_{19} \{\text{M}'(\text{CO})_3\}_m]^{(8-n)-}$ ($\text{M} = \text{Nb, Ta}$; $\text{M}' = \text{Mn, Re}$; $n = 1, 2$). *Inorg. Chem.* **2001**, *40*, 2582–2586. [[CrossRef](#)] [[PubMed](#)]
35. Farges, F.; Brown, G.E.; Rehr, J. Ti K-edge XANES studies of Ti coordination and disorder in oxide compounds: Comparison between theory and experiment. *Phys. Rev. B* **1997**, *56*, 1809–1819. [[CrossRef](#)]
36. Yamazoe, S.; Hitomi, Y.; Shishido, T.; Tanaka, T. XAFS study of tungsten L_1 - and L_3 -edges: Structural analysis of WO_3 species loaded on TiO_2 as a catalyst for photo-oxidation of NH_3 . *J. Phys. Chem. C* **2008**, *112*, 6869–6879. [[CrossRef](#)]
37. Asakura, H.; Shishido, T.; Yamazoe, S.; Teramura, K.; Tanaka, T. Structural analysis of group V, VI, and VII metal compounds by XAFS. *J. Phys. Chem. C* **2011**, *115*, 23653–23663. [[CrossRef](#)]