Base catalytic application of $[Nb_{10}O_{28}]^{6-}$ to CO_2 fixation: A kinetic and theoretical study

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Abstract: The decaniobate cluster $(TBA)_6[Nb_{10}O_{28}]$ (TBA= tetrabutylammonium) was found to act as a Lewis base catalyst for fixation of carbon dioxide (CO_2) to styrene oxide (SO). A kinetic study showed that cycloaddition of CO_2 adsorbed on $[Nb_{10}O_{28}]^{6-}$ with SO corresponded to the rate-determining step in the Eley–Rideal mechanism. We concluded that η–O or μ_2–O sites contributed to the activation of CO_2 on the basis of the adsorption energy of CO_2 on each surface oxygen site estimated by DFT calculation.

Keywords: polyoxometalate, base catalyst, CO_2 fixation.

1. Introduction

Anionic metal-oxide clusters called polyoxometalates (POMs), $[M_xO_y]^{n-}$ (M=V, Nb, Mo, Ta, W), have been widely used as catalysts, especially for acid-catalyzed, oxidation, and photocatalytic reactions. Recently, Mizuno and coworkers reported base catalysis of polyoxotungstates such as $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ and $[WO_4]^{2-}$ for Knoevenagel condensation and CO_2 fixation, respectively [1, 2]. The base catalysis has been ascribed to the negativity of the oxygen atoms. Group V elements (V, Nb, Ta) form more negatively charged POMs than Group VI elements (Mo, W) due to the difference in their maximum oxidation states. This led us to a simple working hypothesis that group V POMs act as a strong base catalyst because of a large negative charge in each oxygen site. Based on this hypothesis, we previously demonstrated that a decaniobate cluster ($[Nb_{10}O_{28}]^{6-}$) showed Brønsted base catalysis for Knoevenagel condensation reaction and ascribed the catalysis to the localized charge on oxygen site estimated from DFT calculation [3]. In this study, we tested the Lewis base catalysis of $[Nb_{10}O_{28}]^{6-}$ for CO_2 fixation to styrene oxide as a representative epoxide. The reaction mechanism was proposed based on kinetic data and the adsorption structures of CO_2 were predicted theoretically.

2. Experimental and Theoretical

$(TBA)_6[Nb_{10}O_{28}]$ (TBA = tetrabutylammonium) was synthesized according to literature procedure with slight modification [4] and was characterized by negative-ion electrospray ionization mass spectrometry (ESI-MS), Nb K-edge X-ray absorption spectroscopy (XAFS), and elemental analysis. Then, it was applied as homogeneous catalyst for CO_2 fixation with styrene oxide (SO). A kinetic study was conducted to shed light on the reaction mechanism by identifying the rate-determining step (RDS). The catalytic reactions were monitored by changing SO concentration ([SO]) and CO_2 pressure (P_{CO2}). To gain an insight into the active site for CO_2 fixation, the geometric structure and charge distribution of the complex of $[Nb_{10}O_{28}]^{6-}$ and CO_2 were studied by DFT calculations.

3. Results and discussion

We found that $[Nb_{10}O_{28}]^{6-}$ acted as a catalyst for CO_2 fixation to SO in the absence of solvent. Time courses of the conversion and selectivity to styrene carbonate (SC) are plotted in Figure 1. The reaction proceeded almost completely in 12 h at P_{CO2} of 0.1 MPa and 403 K. Selectivity to SC remained high (>90%) throughout the reaction, but close inspection revealed that it decreased gradually with time after 4 h.

The kinetic study revealed that the reaction rate R was given as follows:

$$R = k\,[\mathrm{SO}]^{1.06\pm0.04}\, P_{\mathrm{CO2}}{}^{0.88\pm0.05}$$

Based on this equation, we concluded that the reaction proceeded via the Eley–Rideal mechanism in which SO reacted with CO_2 adsorbed on the surface oxygen sites and that the RDS was cycloaddition of adsorbed CO_2 with SO (Figure 2).

The fact that the nucleophilic attack of activated CO_2 to epoxide is the RDS suggested that activation of CO_2 on oxygen site of $[Nb_{10}O_{28}]^{6-}$ was a key to enhance the nucleophilicity of adsorbed CO_2. Therefore DFT calculation was conducted to estimate the adsorption energy of CO_2 on each oxygen site in $[Nb_{10}O_{28}]^{6-}$. Six types of surface oxygen atoms were classified into three in terms of coordination numbers to Nb: η–O, μ_2–O and μ_3–O sites connected to one, two and three Nb atom(s), respectively. Figure 3 showed adsorption energy of CO_2 plotted as a function of localized charge on each oxygen site. No clear correlation was found between the adsorption energy and the negativity of the O sites. The adsorption energy was instead related to the coordination environment and increased with the decrease in coordination number of O sites: η–O > μ_2–O > μ_3–O. The negative charge of CO_2 transferred from $[Nb_{10}O_{28}]^{6-}$ increased with the increase in the adsorption energy, indicating that CO_2 adsorbed with large adsorption energy showed high nucleophilicity. We concluded that η–O and μ_2–O sites acted as Lewis base sites to activate CO_2.

4. Conclusions

We focused on the possibility of group V POM as Lewis base and found that $[Nb_{10}O_{28}]^{6-}$ acted as catalyst for CO_2 fixation to styrene oxide (SO). On the basis of the kinetic study, the reaction was found to proceed via Eley–Rideal mechanism in which cycloaddition of adsorbed CO_2 to SO was the rate-determining step. DFT calculation revealed that the η–O and μ_2–O sites acted as Lewis base site [5].

References

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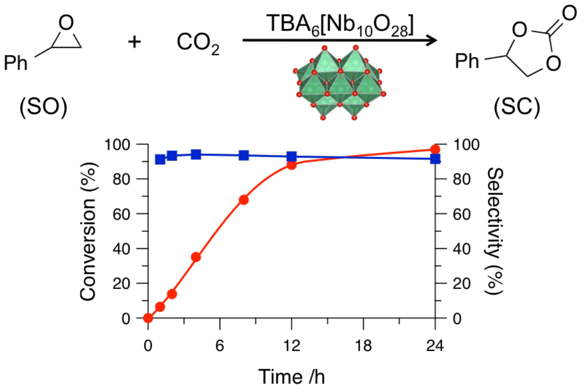

Figure 1. The conversion of SO (red) and selectivity to SC (blue) as a function of reaction time.

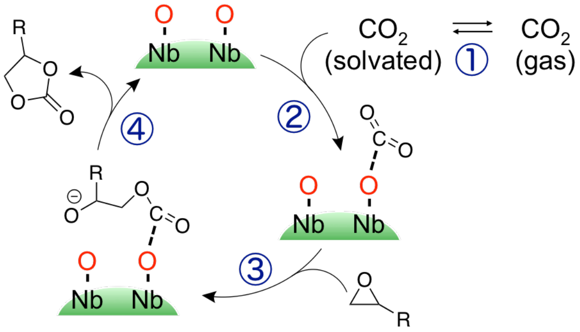

Figure 2. Reaction mechanism of CO_2 fixation to epoxide catalyzed by $[Nb_{10}O_{28}]^{6-}$. Step 3 is the rate-determining step.

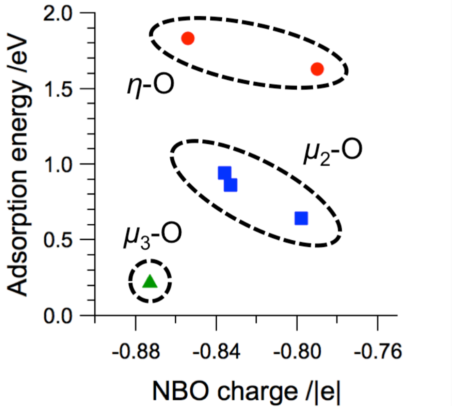

Figure 3. Relationship between NBO charge and adsorption energy of CO_2 for each surface O site.