Host-guest property of half spherical type dodecavanadates

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Abstract: Half spherical type dodecavanadates $[V_{12}O_{32}]^{4-}$ (**1**) possessed a 4.4 Å cavity entrance and several guests were stabilized at the hole. The application of **1** to the reaction fields required the preparation of guest-free type. A guest-free type was isolated and the structure was determined by X-ray crystallographic analysis. One of the bottom VO_5 units was inverted by the removal of a guest. By the vapor diffusion, guests were incorporated into the hole of **1** and the host structure was retrieved. The difference between the guest-incorporated type and the guest-free type was distinguished by IR spectra.

Keywords: Polyoxovanadates, Host-guest chemistry, Alkane conversion.

1. Introduction

Polyoxometalates are a large class of metal–oxygen anion clusters of highly oxidized early transition metal cations of vanadium, molybdenum, and tungsten. They have received much attention in many research fields of science, especially in catalysts because their chemical properties such as redox potentials, acidities, conformations of crystal structures can be finely tuned by choosing structures, constituent elements, and counter cations. Vanadium-based polyoxometalates (polyoxovanadates) show structural versatility due to the variety of the coordination geometries of vanadium such as tetrahedral VO_4, square-pyramidal VO_5, and octahedral VO_6. The square-pyramidal VO_5-based polyoxometalates assemble in spherical structures and it can incorporate anions at the center of the ball. The incorporated guests are stabilized via non-covalent interaction between the vanadium centers and the guests. Dodecavanadates, $[V_{12}O_{32}]^{4-}$ (**1**), possess the half spherical structure and several polar molecules and anions are stabilized at the hole of the structure (Figure 1).[1] The guest exchange of **1** was achieved under the designed conditions, although guests in polyoxovanadates are generally irremovable and unexchangable.[1] In this work, we successfully isolated the guest-free type of **1** (**1-free**) and the uptake of several guests into **1** in the solid state was achieved.

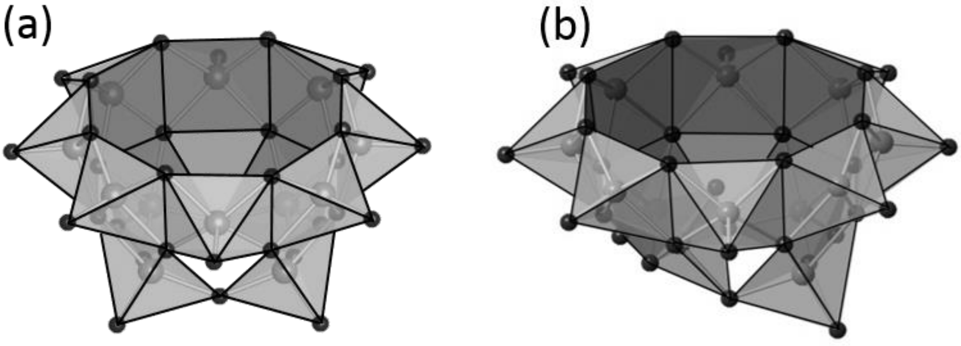

Figure 1. Anion structures of (a) **1** and (b) **1-free**.

2. Experimental

Guest-incorporated dodecavanadates were synthesized by the oxidation of $[(n\text{-}C_4H_9)_4N]_4[V_{10}O_{26}]$ by *t*-BuOOH in the presence of guests. A guest free type of dodecavanadate (**1-free**) was isolated from acetone solution. The molecular structures were determined by the X-ray crystallographic analysis. The guest incorporation reactions were carried out by the vapor diffusion of the guest molecules.

3. Results and discussion

The guest removal of acetonitrile- and 1,2-dichloroethane-incorporated dodecavanadate (**1-AN**, **1-DCE**) required over 100˚C, and the high temperature induced the structure decomposition of **1**. On the other hand, dichloromethane incorporated in **1** was removed under vacuum condition at 50˚C, which was confirmed by ^{1}H NMR spectrum. IR spectrum suggested that the most framework of **1** was retained during the guest removal. The only difference in IR spectra was the intensity of the peak at 840 cm^{-1} due to the V−O−V vibration of bottom part of **1**. With increasing the temperature under vacuum condition, the peak intensity decreased (Figure 2). Fortunately, we successfully isolate the guest-free type of **1** (**1-free**) from acetone solution. The molecular structure of determined by X-ray crystallographic analysis. The whole dodecavanadate structure of **1-free** was resemble to guest-incorporated type of **1** (Figure 1). Although the reported half spherical type dodecavanadates **1** had guest molecules at the hole of the framework, no fragments around the cavity entrance existed in **1-free**. Instead, one of the bottom VO_5 units was inverted and the terminal oxygen atom located near the center of the structure. IR spectrum of **1-free** was identical to the guest-removal dodecavanadate from dichloromethane-incorporated dodecavanadate (**1-DCM**). These results indicated that the oxygen atoms are transfered during the removal of the guest from the framework of **1**.

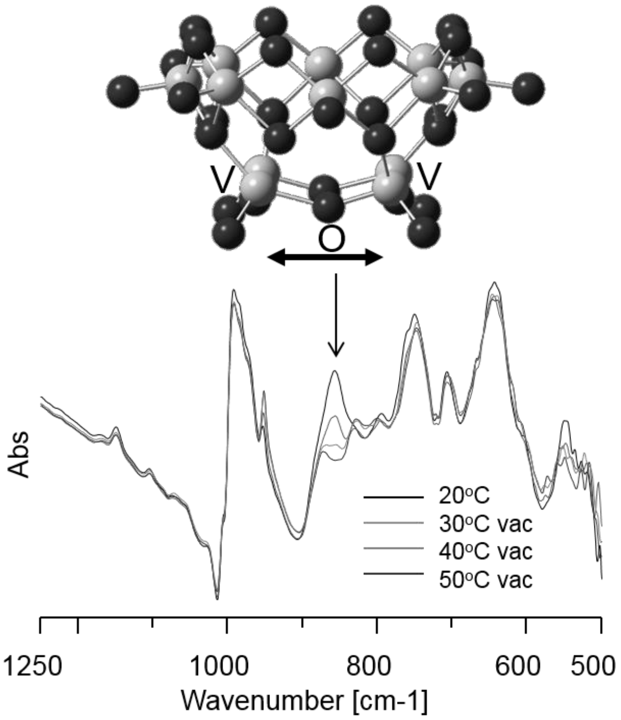

Figure 2. In-situ IR spectra of **1-DCM** under vacuum condition.

From IR spectrum, the inverted VO_5 unit of **1-free** was retrieved to form the original framework of **1**, by the vapor diffusion of dichloromethane, 1,2-dichloroethane, and acetonitrile to the solid state of **1-free**. The powder X-ray diffraction patterns of the samples after the vapor diffusion treatments showed good agreement with the simulated patterns from the single crystal X-ray analyses of **1-DCM**, **1-DCE**, and **1-AN**, respectively. In the guest molecular sorption isotherms showed a step at low vapor pressures and the amount of sorption was 1 mol/mol. This sorption step was probably due to the incorporation of guest molecular into the hole of the framework of **1**. The total amount of sorption was fairly agreed with that determined in the crystallographic analysis.

4. Conclusions

The guest-free type of a half spherical type of dodecavanadate was successfully isolated from the removal of a dichloromethane guest in a solid state and from acetone in a solution state. The guest-free type possess a slightly different molecular structure from the guest-incorporated one and IR spectrum was good probe to distinguish between these two. In the poster presentation, the application of **1** to the reaction field such as alkane conversion will be described.

References

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