

## Polarization of a Bromine Molecule in a Vanadium-Oxide Container

A half-spherical vanadium oxide cluster  $[V_{12}O_{32}]^{4-}$  (V12) has an atomic-sized concavity that can accommodate an anion. From IR and X-ray absorption fine structure analyses,  $Br_2$  was adsorbed in the concavity by exposing V12 to  $Br_2$  gas. The IR-active peak due to the polarized  $Br_2$  was detected at  $185\text{ cm}^{-1}$ . The Br–Br distance was  $2.33\text{ \AA}$ , which is longer than that of  $2.28\text{ \AA}$  in the gas phase. The adsorbed  $Br_2$  in V12 could brominate pentane with a selectivity differing from ordinary bromination. These findings are expected to be useful for the polarization of small molecules and design of highly functional catalysts.

The bromine molecule,  $Br_2$ , is widely used for bromination of a variety of organic compounds. To attain product selectivity different from that of the radical mechanism, it is necessary to control the electron states of the bromine molecule.

Vanadium-oxygen clusters exhibit various kinds of well-defined molecular structures. A particularly intriguing example is half-spherical dodecavanadate,  $[V_{12}O_{32}]^{4-}$  (V12), shown in Fig. 1, which possesses a  $4.4\text{ \AA}$  wide cavity entrance. Half-spherical structures possess multiple interaction sites in a three-dimensionally limited space, unlike simple surfaces of materials and molecules designed with single or double binding sites. The accessibility of external reagents and guests is geometrically controlled to achieve unusual selectivity as reaction fields. V12 shows a unique charge distribution, where the inside is relatively positively charged due to the twelve five-valent vanadium atoms, while the periphery of the cavity entrance is negatively charged due to the eight oxygen atoms. Although V12 has a large negative charge, it offers the stable accommodation of a compound with a negative charge [1]. Among halogen atoms, bromine is the best fit for the concavity [2]. In this study, the adsorption of  $Br_2$  in the concavity of V12, which can induce the polarization of  $Br_2$ , and its

bromination property were investigated [3]. The apex oxygen atom of each  $VO_5$  square pyramid of guest-occupied V12 points outwards. By removing a guest molecule, one of the  $VO_5$  square pyramids at the bottom was flipped inwards, and the flipped  $VO_5$  was retrieved by re-adsorption of a guest molecule [4]. These structural transformations were detected by IR. Guest-occupied V12 showed a strong peak at  $850\text{ cm}^{-1}$  owing to the V–O stretching vibration of the bottom part of V12, whereas the guest-free one showed a weak peak. By exposing the powder of the guest-free type of V12 to  $Br_2$  gas, the peak intensity around  $850\text{ cm}^{-1}$  increased, suggesting the adsorption of  $Br_2$  in the concavity of V12, as shown in Fig. 2(a, b). The X-ray absorption fine structure (XAFS) measurements also support the formation of  $Br_2$ -occupied V12. Figure 2(c) shows the Fourier transform magnitude of radial distribution functions for the vanadium K-edge extended XAFS (EXAFS) spectra. Guest-occupied V12 and the guest-free one substantially reflect the distribution of the bond distances in their crystal structures. The result of the sample after exposing the guest-free type of V12 powder to  $Br_2$  is similar to that of the guest-occupied V12 rather than that of the guest-free one.

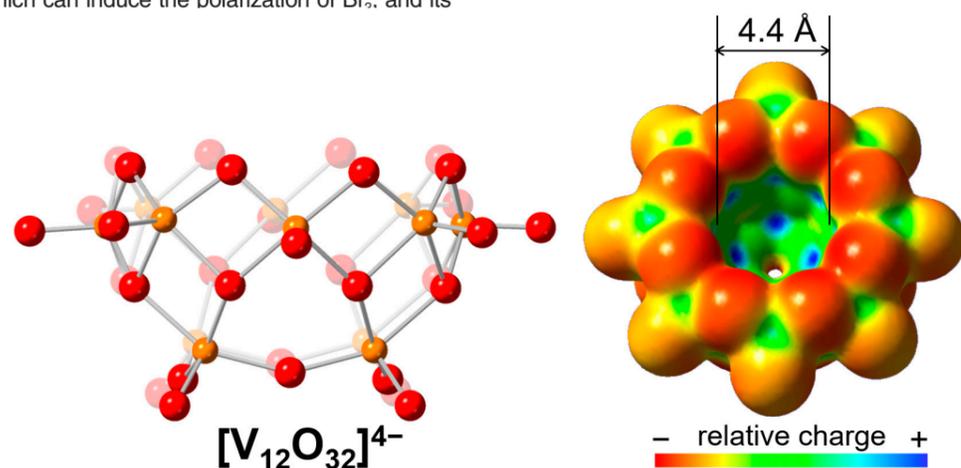


Figure 1: Molecular structure and charge distribution of guest-occupied V12. The guest molecule is omitted for clarity. Orange and red spheres in the ball and stick model represent vanadium and oxygen atoms, respectively.

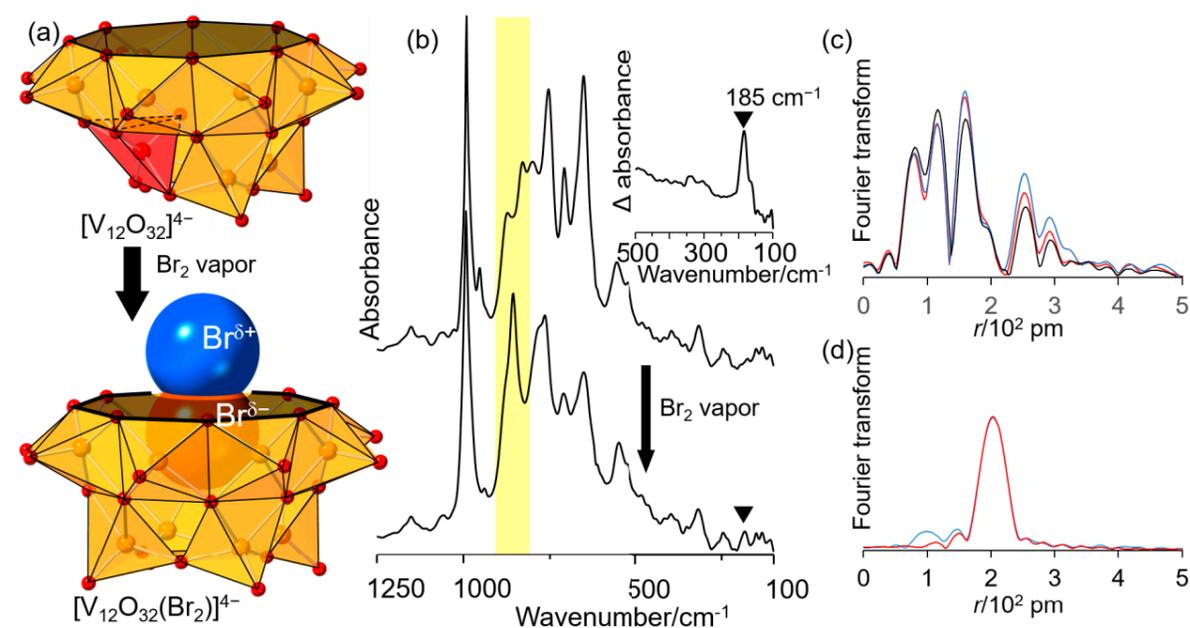


Figure 2: (a) Polyhedral model representation of the guest-free type of V12 and  $Br_2$ -occupied V12. The red square pyramid represents the  $VO_5$  unit flipped inwards. (b) IR spectra of the guest-free type of V12 before and after exposure to  $Br_2$  vapor. The highlight represents the characteristic region to determine the guest-free type of V12 (weak) and the guest-occupied one (strong). The insertion is represented by the difference spectrum. The peak at  $185\text{ cm}^{-1}$  is due to the polarized Br–Br vibration. (c) V K-edge EXAFS data. Red, blue and black lines represent the spectra of  $Br_2$ -occupied V12, guest-occupied one and guest-free one, respectively. The peak intensity ratio of the second to third peaks is different between guest-occupied V12 and the guest-free one. (d) Br K-edge EXAFS data. Blue and red lines represent experimental and fitted spectra, respectively.

In the IR spectrum, an absorption peak at  $185\text{ cm}^{-1}$  originating from polarization of  $Br_2$  was observed, although  $Br_2$  without polarization would not show such a peak. This is the first report on spectroscopic evidence of polarized  $Br_2$ . The bromine K-edge EXAFS spectrum shown in Fig. 2(d) suggests a Br–Br distance of  $2.33\text{ \AA}$ , which is longer than that in gas-phase  $Br_2$  ( $2.28\text{ \AA}$ ). The reactivity of  $Br_2$ -occupied V12 with toluene, yielding ring-brominated products as the main products, also supported the polarization of  $Br_2$ . For reference, addition of liquid  $Br_2$  to toluene produced benzyl bromide as the main product via a radical reaction mechanism.

Using  $Br_2$  in the concavity of V12 as a bromine source, bromination of pentane yielded 2-bromopentane and 3-bromopentane in a ratio of 36:64, which differs from the ratio of 80:20 when bromination was carried out in the absence of V12. In addition, among monobromopentane, 2-bromopentane was selectively reacted to form a *threo* isomer of 2,3-dibromopentane with higher selectivity than when  $Br_2$  alone was reacted. Furthermore, bromination could take place with smaller alkanes with shorter carbon chain such as butane or propane.

In conclusion, it was found that the  $Br_2$  trapped in the atomic-sized concavity was polarized and showed a specificity different from the radical mechanism for bromination reaction of alkanes. Further developments

are expected such as the activation of small molecules using such an atomic dimension cavity through controlling the charge distribution in the concavity and the production of highly functional catalysts by controlling molecular-level structures. It is also expected that selective functionalization reactions using methane, which is highly inert but whose efficient chemical modification is highly desirable, can be attained by improving materials that regulate the electron states.

### REFERENCES

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### BEAMLINE

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