STRUCTURAL DYNAMICS OF LACUNARY POLYOXOMETALATE $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ ACTIVATED WITH H_2O_2 ELUCIDATED BY *IN SITU* ATR-IR AND VIBRATIONAL CALCULATIONS

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Olefin epoxidation is a significant reaction because epoxides can offer a variety of products, such as polyurethane, epoxy resin, and ethylene glycol. Catalytic epoxidation with H_2O_2 attracted attention because only water is generated as a byproduct. Polyoxometalates (POMs), anionic metal oxide clusters, was reported as one of the most promising catalysts [1]. Kamata and coworkers reported that a lacunary POM ($TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$: **1**) functions as a homogeneous catalyst in acetonitrile and as a heterogeneous catalyst in ethyl acetate for the olefin epoxidation reaction [2-4]. **1** reacts with H_2O_2 to form a peroxo species ($TBA_4[\gamma\text{-}SiW_{10}O_{32}(O_2)_2]$: **2a**), whereas it was suggested that the hydroperoxo species ($TBA_4[\gamma\text{-}SiW_{10}O_{32}(O_2)(OOH)]$: **2b**), which can serve as a proton donor, contributes to the catalytic reaction. However, the structure of peroxo and hydroperoxo species remains unclear.

In this work, we investigated the molecular structure of peroxo and hydroperoxo species in lacunary POMs using *in situ* ATR-IR and DFT studies (Figure 1(a)). **1** was synthesized by a previously reported method [4]. ATR-IR spectra were recorded by depositing **1** on the ZnSe prism and flowing the ethyl acetate solution added with 60wt% H_2O_2 aq. at the flow rate of 1 mL/min.

Figure. 1(b) show *in situ* ATR-IR spectra obtained at 60 ºC of **1** 3.5 minutes and 35 minutes after the addition of ethyl acetate and H_2O_2. **1** was used as the background. These results reveal that the structure undergoes a structural change upon reaction with H_2O_2, and additional changes depending on the existence of H_2O_2. Vibrational frequency and intensity calculations using DFT were performed assuming peroxo and hydroperoxo species in the lacunary POMs. The spectrum obtained after 35 min matched that of the hydroperoxo species from the vibrational calculations, while the spectrum after 3.5 min matched that of the peroxo species from the vibrational calculations. These results suggest that during the reaction with H_2O_2,, the intermediate exists in the structure of **2a**, while the product exists in the structure of **2b**.

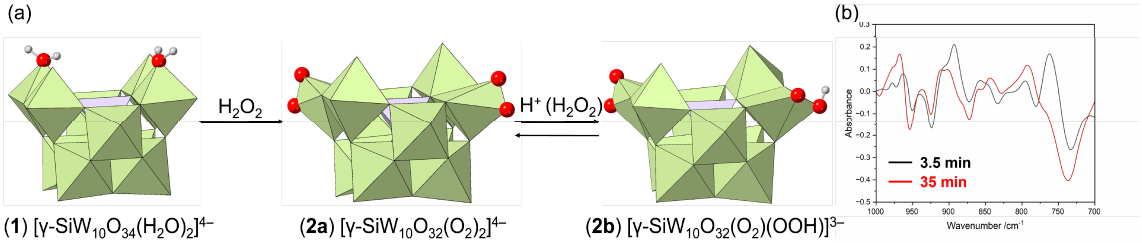

Figure. 1 (a) Schematic illustration of the anionic part of **1**, **2a,** and **2b** (b) *in situ* ATR-IR spectra flowing with the ethyl acetate and H_2O_2 solution at 60 ºC.

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[2] K. Kamata *et al.*, *Science*, 300, (2003) 964.

[3] K. Kamata *et al.*, *Chem. Eur. J.*,13, (2007) 639.

[4] S. Uchida *et al.*, *Dalton trans*, 41, (2012) 9979.