

## Near-IR spectroscopy to monitor the epoxidation reaction between cyclic olefin and peroxide species

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Adsorption states of alkenes on various catalysts have been investigated by IR spectroscopy. In this study, we have focused on an advantage of near-IR (NIR) spectroscopy to clarify different adsorption states of alkenes on various cation sites. Adsorption states of alkenes (ethylene, hexene, and cyclooctene) on various cation-exchanged ZSM-5 and Ti-containing mesoporous silica have been investigated by NIR spectroscopy. Furthermore, the NIR spectroscopy can clarify the differences between peroxide species, alcohol and water molecules. We have tried to investigate the mechanism for epoxidation reaction of alkene with peroxide species.

ZSM-5 zeolites (cations;  $\text{Na}^+$ ,  $\text{Ag}^+$ , and  $\text{H}^+$ ) and Ti-SBA-15 were used. The pellet samples were placed in an in-situ IR-cell and pretreated at 723 K. Ethylene was admitted in the cell, step by step. NIR spectra of ethylene adsorbed on the samples were recorded by using a FT-IR spectrophotometer in a diffuse reflectance mode. Furthermore, NIR spectra of cyclooctene and TBHP were recorded in the same procedure.

Figure 1 shows the NIR spectra of ethylene adsorbed on the ZSM-5. Two typical absorption bands due to ethylene were observed at around 4700 and 4500  $\text{cm}^{-1}$ . These bands can be assigned to  $[\nu_{\text{=CH}_2} + \nu_{\text{C=C}}]$  and  $[\nu_{\text{=CH}_2} + \delta_{\text{=CH}_2}]$  combination bands, respectively. It was notable that the former band was dependent to different cation sites. The ethylene adsorbed on  $\text{Na}^+$  site was observed at 4698  $\text{cm}^{-1}$ . However, the absorption band of ethylene on  $\text{Ag}^+$  sites shifted to 4670  $\text{cm}^{-1}$ . This red shift indicates the stabilization of ethylene molecules interacting with  $\text{Ag}^+$  sites. In the case of  $\text{H}^+$ /ZSM-5, the typical absorption bands due to ethylene were hardly observed. This result suggests the formation of protonated species on  $\text{H}^+$  sites.

Next, Fig. 2 shows the NIR spectra of cyclooctene and TBHP on the Ti-SBA-15. First, ethylene was adsorbed on the catalyst, followed by adsorption of TBHP. In this procedure, cyclooctene and peroxide species were observed at 4665 and 4861  $\text{cm}^{-1}$  at the same time (2c). When the sample was heated at 333 K (d, e), the band due to cyclooctene (4665  $\text{cm}^{-1}$ ) disappeared. However, when TBHP was first adsorbed on the catalyst, followed by adsorption of cyclooctene, only the NIR band due to TBHP was observed (spectra not shown here). These results clearly suggest the simultaneous adsorption of alkene and peroxide species is quite important for an epoxidation reaction.

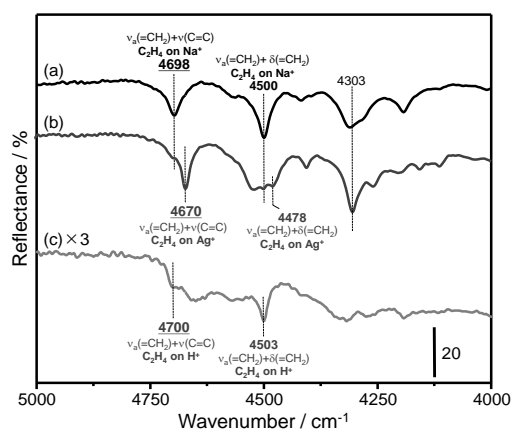


Fig. 1 NIR spectra of ethylene adsorbed on (a)  $\text{Na}^+$ /ZSM-5, (b)  $\text{Ag}^+$ /ZSM-5 and (c)  $\text{H}^+$ /ZSM-5.

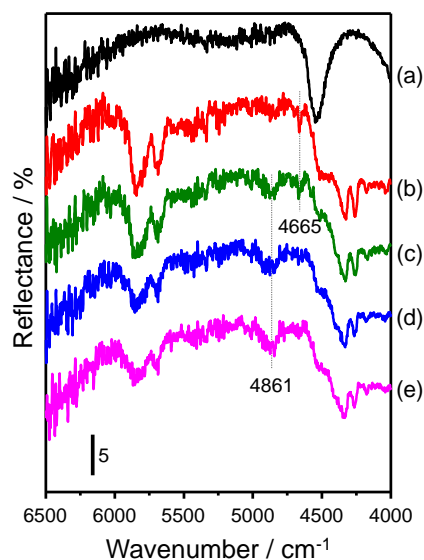


Fig. 2 NIR spectra of cyclooctene and TBHP adsorbed on Ti-SBA-15. (a) after pretreatment, (b) cyclooctene adsorption, (c) TBHP adsorption, (d, e) 333 K for 1 and 10 mins.