NIR spectroscopy for the NH_3 and NH_4^+ species adsorbed on various zeolites

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Brönsted or Lewis acid sites of various zeolite have been widely characterized by NH_3-TPD, NH_3-IR, pyridine-IR and so on. However, the stretching and bending modes of NH_3 and NH_4^+ are closely observed to those of H_2O molecule. That is, MIR spectra of the NH_3 or NH_4^+ adsorbed on catalyst surfaces are generally measured for dehydrated samples. In contrast, NH_3, NH_4^+, and H_2O species show different NIR absorption bands at around 5000, 4800 and 5200 cm^{-1}, respectively. This advantage makes it possible to detect NH_3 or NH_4^+ species even on hydrated catalyst surfaces. From this viewpoint, we have investigated the adsorption states of NH_3 and/or NH_4^+ species on various dehydrated and hydrated zeolite surfaces.

Various cation-exchanged ZSM-5 (cations; H^+, Na^+, Cu^{2+}, Ni^{2+}) were used in this study. The pellet samples were placed in an in-situ IR-cell and pretreated at 723 K. NH_3 gas was then admitted into the cell, step by step. NIR spectra of NH_3 and/or NH_4^+ adsorbed on the zeolites were recorded by using a FT-IR spectrophotometer in diffuse reflectance mode.

Figure 1 shows the NIR and MIR spectra of various ZSM-5 zeolites. H_2O, NH_3 and NH_4^+ could be independently observed in NIR region. Figure 2 shows the NIR spectra of NH_3 and NH_4^+ species adsorbed on various cation-exchanged ZSM-5 zeolites. When NH_3 was adsorbed on the Na^+/ZSM-5, the NIR absorption bands were observed at 5020 and 4560 cm^{-1} (2a). These bands can be assigned to ($\nu_3+\nu_4$) and ($\nu_2+\nu_3$) combination bands of hydrogen-bonded NH_3 cluster. In the case of H^+/ZSM-5, the NIR absorption bands were observed at 5035 and 4840 cm^{-1} (2b). These bands can be assigned to ($\nu_3+\nu_4$) of isolated NH_3 and ($\nu_2+\nu_3$) of isolated NH_4^+ formed on the H^+ sites, respectively. Interestingly, as the NH_3 adsorption amounts increased, these bands shifted to 5017 and 4782 cm^{-1}, because of the formation of hydrogen-bonded NH_3 and NH_4^+ species. Furthermore, when NH_3 was adsorbed on Cu^{2+}/H^+/ZSM-5 (2c) and Ni^{2+}/H^+/ZSM-5 (2d), NH_3 molecules highly stabilized on Cu^{2+} or Ni^{2+} sites could be observed at around 4960 cm^{-1}.

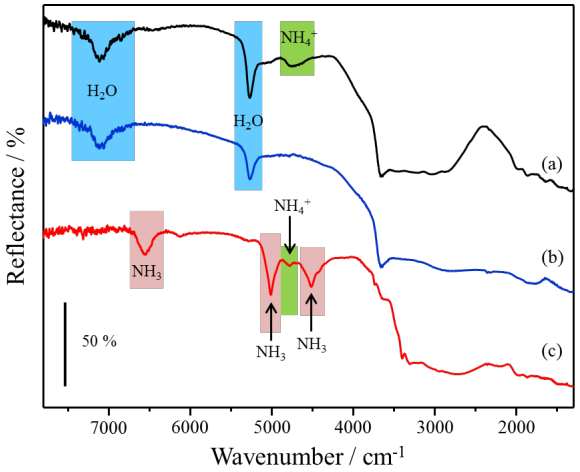

Fig. 1 Near and middle IR spectra of (a) NH_4^+/ZSM-5 (measured in air), (b) H^+/ZSM-5 adsorbed with H_2O, and (c) H^+/ZSM-5 adsorbed with NH_3.

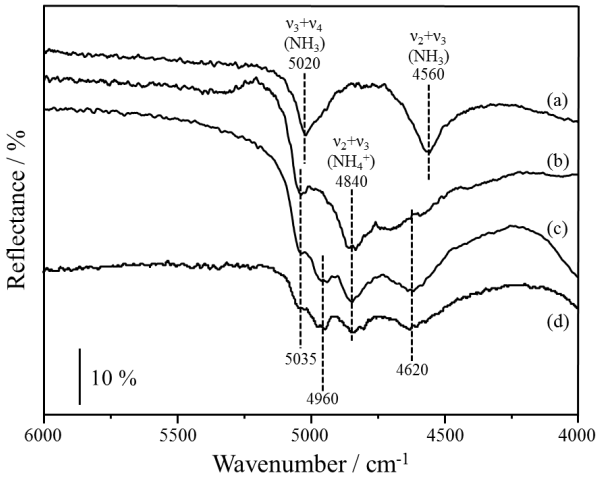

Fig. 2 NIR spectra of NH_3 and/or NH_4^+ species adsorbed on (a) Na^+/ZSM-5, (b) H^+/ZSM-5, (c) Cu^{2+}/H^+/ZSM-5, (d) Ni^{2+}/H^+/ZSM-5, (after degassed at 423 K), Cu^{2+}, Ni^{2+}: 1.0 wt% SiO_2/Al_2O_3 ratios: (a, c, d) 23.8, (b) 39.0

REFERENCES

[1] M. Takeuchi, et. al., "Investigation of NH_3 and NH_4^+ adsorbed on ZSM-5 zeolites by near and middle infrared spectroscopy", Catal. Sci. Technol., 5, 4587 (2015).