Design of hydrophobic zeolite material by modification using triethoxyfluorosilane and its application as a Support of TiO$_2$ Photocatalyst

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Introduction
Nano-size TiO$_2$ particles formed on zeolite cavities can show efficient adsorption and photocatalytic degradation of organic pollutant diluted in liquid or gaseous phases [1]. In the previous studies, it has been verified that the photocatalytic property of degradation of organic compounds much depends on the hydrophilic-hydrophobic properties of zeolite surface originated from SiO$_2$/Al$_2$O$_3$ ratio and number of surface silanol group. In this study, we offer a simple method to design highly hydrophobic zeolite through surface modification using triethoxyfluorosilane (TEFS) reagent and assess the efficiency of this material as a support of TiO$_2$ photocatalyst. The investigation of local structure of titanium oxide species on the modified zeolite surface was conducted by X-ray absorption fine structure (XAFS).

Experimental
The Y-zeolites with various SiO$_2$/Al$_2$O$_3$ ratio were stirred in the triethoxyfluorosilane (TEFS) solution dissolved in 2-propanol for 3 h. The suspensions were dried and calcinated at 773 K for 5 h to obtain FS$n$-Y zeolite, where $n$ ($n$=1, 2 and 4) means the molar ratio of TEFS reagent, 10, 20 and 40 respectively. The prepared samples were characterized by XRD, water adsorption measurements and BET surface area measurement. Furthermore, we applied these surface modified zeolites as the supports of TiO$_2$ photocatalysts and assessed their efficiency. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K. The Fourier transform was performed on $k^2$-weighted EXAFS oscillations in the range of 3–10 Å$^{-1}$. In a typical experiment, the sample was loaded into the in situ cell having the plastic windows.

Results and discussions
The microporous structure and the surface area had been maintained even after the modification process and these modification zeolites were found to be thermally stable. Water adsorption capacities per unit surface area dramatically decreased according to the TEFS ratio.

Fig. 1 shows the results of Ti K-edge XAFS analyses of TPOT, TiO$_2$ anatase crystal as reference samples and TiO$_2$ loaded on FS$n$-Y samples. One sharp preedge peak at around 4970 eV observed in the XANES spectrum of TPOT originate from the isolated titanium oxide species surrounded by four oxygen atoms in the zeolite framework. And the peaks at around 2.5 Å in the FT-EXAFS spectra due to the Ti-O-Ti bond of titanium oxide crystal [2]. Ti K-edge peak of TiO$_2$/Y showed medium intensity between isolated titanium species and bulk TiO$_2$, suggesting that the zeolite mesoporous structure might restrict crystallization of TiO$_2$. On the contrary, Ti K-edge peak of TiO$_2$/FS4-Y showed much closer spectra to bulk type TiO$_2$ in both XANES and EXAFS spectra, suggesting that well-crystallized TiO$_2$ particles were obtained in surface modified pores. This is attributed to smaller interaction between the modified surface and the transferred titanium species because of decrease in amount of surface hydroxyl groups. Consequently, it is thought that the titanium species were aggregated and the crystallization of TiO$_2$ was promoted in the modified zeolite pores.

It was also found that these modified zeolites can adsorb organic compounds diluted in water efficiently and the photocatalytic activities were highly enhanced due to its hydrophobicity brought about by TEFS modification.

Conclusions
It was demonstrated that the surface modification using TEFS is a promising way to modify zeolite to have surface hydrophobicity. These surface modified zeolites are suitable as the supports of TiO$_2$ photocatalyst and can promote the crystal growth of TiO$_2$ and enhance photocatalytic degradation of organics diluted in water because of removal of surface hydroxyl groups.

References
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