

# Design of hydrophobic zeolite material by modification using triethoxyfluorosilane and its application as a support of TiO<sub>2</sub> photocatalyst

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## Introduction

Zeolite with large surface area and microporous structure has been attempted to be utilized as a new type of material in photochemical fields for its condensation property as a conventional adsorbent. Especially, small isolated TiO<sub>2</sub> particles loaded on zeolite have been attractive for its efficient adsorption and photocatalytic degradation of organic pollutant diluted in liquid or gaseous phases [1,2]. In the previous studies, it has been demonstrated that the photocatalytic property of degradation of organic compounds much depends on the hydrophilic-hydrophobic properties of zeolite surface deriving from SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and number of surface hydroxyl groups. In the case of zeolite with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, water in liquid or gaseous phase is adsorbed preferentially by the interaction with the surface hydroxyl groups. Hence the zeolite with higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and zeolite including fluorine can be used as the useful support for the high ability in the adsorption of organics [3].

In the present study, therefore, the surface modified hydrophobic zeolites were prepared by using triethoxyfluorosilane (TEFS) as fluoride containing silylation agent. This agent was employed for its ability to terminate surface hydroxyl groups and to form robust silica bonding on the surface. Y-zeolite with various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio were employed as substrate zeolites to evaluate their influences. The adsorption properties and surface condition of the prepared fluoride-modified hydrophobic zeolites were characterized. Furthermore, these zeolites were applied as the supports of TiO<sub>2</sub> photocatalysts and the photocatalytic properties for the degradation of various organics were studied.

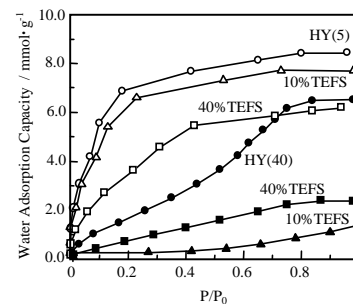
## Materials and Methods

The surface modification process was performed by impregnating Y-zeolite to triethoxyfluorosilane (TEFS) solution diluted in 2-propanol which prevents TEFS condensation in moisture, followed by calcined at 773 K. The ratio of TEFS to zeolite was changed to 0, 10, 20, 40 mol% and the prepared samples were characterized by XRD, adsorption measurements with water and organics, BET surface area measurement and FT-IR spectroscopy. The preparation of TiO<sub>2</sub> particles loaded on the zeolite samples was carried out by an impregnation method. The surface modified Y-zeolite was stirred in ammonium titanil oxalate ((NH<sub>4</sub>)<sub>2</sub>[TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·nH<sub>2</sub>O) solution to be followed by evaporation and calcination at 773 K. The local structures of titanium oxide species loaded on the fluoride-modified zeolites were investigated by X-ray absorption fine structure. The Ti K-edge XAFS measurements were recorded at 295 K in fluorescence mode at the BL-9A facility of the Photon Factory. The influences of the modification for photocatalytic activity were evaluated by the degradation of organics diluted in water under UV-light irradiation at room temperature.

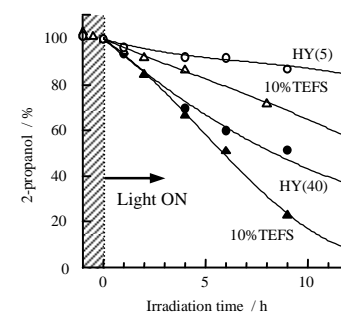
## Results and Discussion

The zeolite with ordered microstructure and large surface area were maintained even after the surface modification. The prepared samples were thermally stable at the temperature of calcination (773 K). As shown in the Fig. 1 the ability of water adsorption of zeolite after the surface fluoride-modification decreases and the effects of modification are observed to be different depending on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of zeolites. It was also found that these modified zeolites can adsorb organic compounds diluted in water efficiently.

The time profiles of the photocatalytic degradation of 2-propanol diluted in water are shown in Fig. 2. The TiO<sub>2</sub> photocatalyst loaded on the fluoride-modified zeolites exhibited higher photocatalytic reactivity than those loaded on the original Y-zeolites. The higher photocatalytic reactivity was observed with the catalyst modified with the larger amount of TEFS. These results indicate that the modified zeolites are more suitable as the supports of TiO<sub>2</sub> photocatalyst and can enhance the photocatalytic degradation of organics diluted in water, because of the ability to interrupt H<sub>2</sub>O molecule adsorption in water.



**Figure 1.** The adsorption isotherms of H<sub>2</sub>O molecules at room temperature of standard Y-zeolites and surface modified Y-zeolites. (○ : SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=5, △ : SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=40)



**Figure 2.** Reaction time profile for the photocatalytic degradation of 2-propanol diluted in water on 10wt% TiO<sub>2</sub> loaded on Y-zeolites.

## Significance

The hydrophobic surface modification of zeolite nano-porous material could be realized using TEFS agent and this fluoride-modified zeolite was suitable as the support of TiO<sub>2</sub> photocatalyst for degradation of organics diluted in water.

## References

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2. H. Yamashita, K. Maekawa, H. Nakao, M. Anpo, *Appl. Surf. Sci.*, **237**, 393 (2004).
3. K. Ikeue, H. Yamashita, M. Anpo, *J. Phys. Chem. B*, **105**, 8350 (2001).