# $TiO_2$/ZSM-5 composite photocatalyst: effects of zeolitic crystal size and acidity on photocatalytic activity in the degradation of azo dye

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## Introduction

$TiO_2$-based photocatalysts have been extensively investigated in order to achieve better efficiency. The dispersion of $TiO_2$ on supports has become attractive, because it can stabilize fine $TiO_2$ particles and merge the supports' adsorption ability into the resulted composite photocatalyst. Fine $TiO_2$ particles can help to slow down the recombination rate of the electron-hole pairs generated in the valence band and conduction band of $TiO_2$ semiconductor [1]. The adsorption function of the supports can concentrate the reactant molecules from either liquid-phase or gas-phase to the vicinity of supported $TiO_2$ photoactive sites [2]. Obviously, these must facilitate the photocatalysis of $TiO_2$.

So far, the dispersion of $TiO_2$ on several zeolites and molecular sieves such as ZSM-5, Y, β and MCM-41 has been reported. However, to the best of our knowledge, the effects of zeolitic crystal size and acidity on the dispersion of $TiO_2$, the adsorption behavior and photocatalytic efficiency of the composite photocatalyst have not yet been addressed. Therefore, in this presentation, we focus on these issues by using a series of ZSM-5 zeolites with different crystal sizes (different external surface areas), and a series of ZSM-5 zeolites with different sodium-ion contents (different acidities).

## Materials and Methods

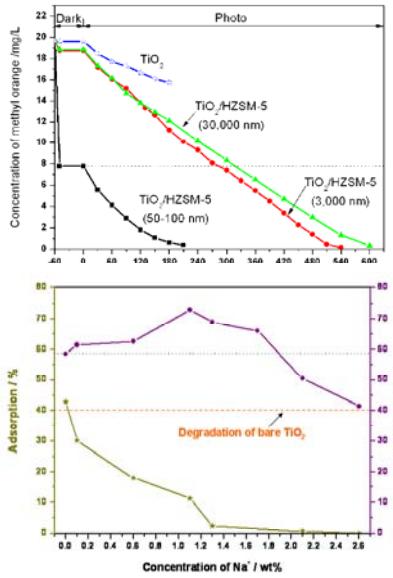
Zeolites with different crystal sizes were hydrothermally synthesized in our laboratory. Their $SiO_2/Al_2O_3$ ratios fall inside 50-60 (mole), but crystal size ranges from 50 to 30,000 nanometers. Zeolites with different sodium-ion contents were obtained by impregnating a nano-HZSM-5 zeolite ($SiO_2/Al_2O_3$ = 28 (mole), crystal size = 20-50 nm) with $NaNO_3$ solutions of different concentrations. The dispersion of $TiO_2$ on the zeolitic supports was accomplished with a self-developed controlled sol-gel process characterized by pre-adsorbing a desired amount of deioned water into the micropores of nano-zeolites, and characterized by HRTEM; the total $TiO_2$ loading was analyzed by XRF and ICP, and the surface $TiO_2$ content was measured by XPS; the photoresponse of the photocatalysts was characterized with UV-vis spectra; the acidity of the photocatalysts was measured by $NH_3$-TPD and pyridine-FTIR; the adsorption behavior and the photocatalytic efficiency of the photocatalysts were assessed with dilute methyl orange (MO) solution. UV light was used for irradiation source.

## Results and Discussion

We observed that, by using the self-developed controlled sol-gel process $TiO_2$ can be planted on the external surface of ZSM-5 zeolites preferentially, and evenly distributed small $TiO_2$ particles were favored. However, at the same $TiO_2$ loading, the composite photocatalysts using smaller crystal ZSM-5 as supports always showed larger adsorption capacity and higher photocatalytic efficiency in the degradation of MO. This is attributed to the larger external surface areas of smaller ZSM-5 zeolitic supports. As the sodium content of the zeolitic support grew, its strong acid sites decreased gradually due to the replace of $H^+$ by $Na^+$(Fig.3 high-temp. peak), which was accompanied by the reduction of MO adsorption capacity. This indicates that the adsorption of alkaline methyl orange molecules mainly takes place on strong acid sites of zeolitic surface. Surprisingly, the efficiency of photocatalyst increased with the reduction of MO adsorption capacity and showed maximum at Na% = 1.1, where the adsorption of MO occurred on medium-strong acid sites and was near completely reversible.

## Significance

Results in this presentation shows, for the first time, the advantage of a nanosized crystal zeolite in preparing supported photocatalyst that has high $TiO_2$ dispersion at high $TiO_2$ loading and reserves largely the support's original adsorption capacity, and the importance of tuning the physicochemical properties of support in enhancing the synergic effect of adsorption and photocatalysis. Therefore, this study might be helpful for the improvement of $TiO_2$ photocatalysts.



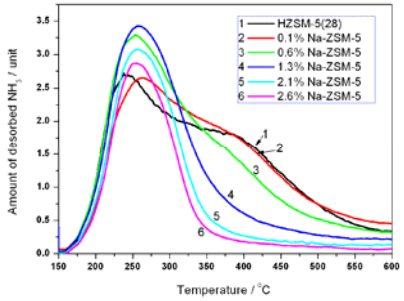




Fig. 1 Effect of the crystal size of ZSM-5 zeolite support on the adsorption capacity and catalytic activity of composite photocatalysts (left top).

Fig. 2 $NH_3$-TPD profiles of nano-HZSM-5 zeolite support with different $Na^+$ contents (right top).

Fig. 3 Effects of Na+ content in zeolite support on the adsorption and photodegradation of MO (left bottom).

## References

1. Ooka, C., Yoshida, H., and Horio, M., et al., *Appl. Catal. B: Environ.* 313, 41 (2003).
2. Takeuchi, M., Kimura, T., and Hidaka, M., et al., *J. Catal.* 235, 246 (2007).

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