Photoreduction of Methyl Orange Catalyzed by Nile Red-Adsorbed TiO$_2$ / Y Zeolites using Visible Light

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Photoreduction of Methyl Orange was investigated by using Nile Red-adsorbed TiO$_2$ / Y zeolites. Nile Red was successfully adsorbed on TiO$_2$ / Y zeolites and the absorption profile is very broad with maxima, ca. 630 nm. The peak is largely red-shifted compared to that observed in hydrocarbon solvents. Furthermore, a broad and largely Stokes shifted emission band as observed around 660 nm. The largely Stokes shifted emission band should be originated from the excited state structural changes. In order to understand the photocatalytic activities of Nile Red-adsorbed TiO$_2$ / Y zeolite, the photoreduction of Methyl Orange ($5.0 \times 10^{-5}$ M) was studied using visible light beyond 320 nm. Methyl Orange was effectively reduced by Nile Red-adsorbed TiO$_2$ / Y zeolite, indicating the photocatalytic activity of Nile Red-adsorbed TiO$_2$ / Y zeolites was enhanced by about eight times higher than that of TiO$_2$ / Y zeolite.

Key words: photocatalyst, TICT(twisted intramolecular charge transfer), Nile Red, TiO$_2$ / Y zeolite

INTRODUCTION

Interfacial photochemical reaction on the surface of TiO$_2$ particles as semiconductor has attracted much interest because of its potentiality in developing high conversion of solar energy into chemical energy, degradation of pollutants, and so on [1-3]. The principal use of small semiconducting particles is as a source of electrons ($e^-$) and holes ($h^+$) created by the absorption of light. After excitation of TiO$_2$, the photogenerated electrons migrate from valence band to conduction band which the generated holes in void site of valence band, followed by their participation in the electron transfer reaction with adsorbed molecules [4]. In competition with this process, however, electron-hole recombination should take place within femtosecond and picosecond regions in a TiO$_2$ particle [5-8]. For example, Bowman R. M et al. have reported that the photogenerated electron of conduction band in the TiO$_2$ colloidal system become rapidly trapped, and subsequently undergo electron-hole recombination within the first 50 ps [9]. Such a rapid electron-hole recombination diminishes the overall efficiency of photoactive TiO$_2$ particles.

For the control of electron transfer processes like the quick electron-hole recombination, the preparation of introducing Ti species directly into Y zeolites with large 13 Å supercages connected 7.4 Å windows through the common ion exchange procedures using an aqueous solution of (NH$_4$)$_2$TiO(C$_2$O$_4$)$_2$H$_2$O [10]. To increase the efficiency of TiO$_2$ particles as photocatalyst, we make an attempt to encapsulate TiO$_2$ particles in zeolites. Recently, zeolites have been used as hosts to fix semiconductors because they offer unique of reaction fields nanoscaled pores [10-12]. Because the zeolites have void shape-selective cavities and the pores sizes are similar to those of generally organic molecules, these TiO$_2$ particles encapsulated within Y zeolites isolates the photosensitive organic molecules. Finally, TiO$_2$/Y zeolites are effective in the utilization of sunlight. In our previous work, we have reported the new photocatalytic system that combine the TiO$_2$/Y zeolite with p-$N,N'$-dimethylaminobenzoic acid(DMABA) as an intramolecular charge transfer(ICT) molecule [13]. Through these studies we have found that this photocatalytic system has enhanced the photocatalytic efficiency as well as the recovery efficiency. Nevertheless, DMABA has a limitation to absorb a UV (ultraviolet) light below 320 nm that is no more than 5% of sunlight.

In the present work we attempted to use Nile Red to encapsulate into the TiO$_2$/Y zeolites to utilize effectively the whole solar light without loss of energy in which particular photoresponse to visible light. Nile Red is an excellent candidate for sensing applications since it is highly solvatochromic, i.e., exhibits wavelength shifts in both absorbance and emission bands in the presence of various molecules [14]. Chemisorption of the sensitization dye on the surface of the wide band gap semiconductors such as titanium dioxide plays an important role in the sensitization efficiency. J. Cherepy et al. have designed successfully an efficient and stable solar cell by using semiconductor films consisting of nanometer sized TiO$_2$ particles and charge transfer dyes [3]. The dye is typically adsorbed on the surface of the semiconductor particles and acts as an electron donor, injecting electrons from the excited state Nile Red into the conduction band of the semiconductor under visible light irradiation. Instead of the TiO$_2$ particles, we
have used the TiO$_2$/Y zeolites to support the Nile Red to develop the new photocatalyst responding to the visible light. The new photocatalyst system must be improved in its quantum efficiency, too.

**MATERIALS AND METHODS**

**Material.** The HY zeolite was prepared by ion-exchanging with the NaY zeolite (Si/Al = 2.47) with 0.1 M NH$_4$Cl [15]. Titanium-exchanged zeolites were prepared from HY zeolites with an aqueous solution of ammonium titanyl oxalate monohydrate, (NH$_4$)$_2$TiO(C$_2$O$_4$)$_2$H$_2$O (Aldrich Chemical Co.) as described by Liu, Lu and Thomas [10,15]. The ion-exchanged zeolite has 7.2 Ti species each unit cell. The titanium-exchanged zeolites were washed with the triply distilled water several times to remove the chemicals, which were adsorbed on external surface, and dried with air suction. The sample was then calcinated at 450°C for 6 h. The temperature of the sample was elevated with a rate of 1.67 °C/min. The sample was cooled down by decreasing the temperature with the same rate as the temperature increased. The TiO$_2$/Y zeolite were transferred to a pyrex cell and activated at 230-240 °C for 2 h under vacuum (10$^{-4}$ torr), then shaken with 10 ml of degassed acetonitrile solution containing 1.0 $\times$ 10$^{-3}$ M Nile Red for 12 h. To remove acetonitrile, the solid was dried in vacuum. The dried solid was transferred to quartz cell under the same vacuum for the spectroscopic measurements.

**Experimental methods.** The X-ray diffractograms were recorded on MO3X-HF diffractometer (Model-1031, Mac Science Co.). To measure the IR spectra, JASCO FT/IR-410 spectrometer and KBr technique were used. Diffuse reflectance UV-vis spectra were recorded by using a Shimadzu UV-3101PC spectrometer equipped with an integrating sphere. Absorption spectra were measured on a SHINCO UVS 2040 spectrometer. Diffuse reflectance fluorescence measurements were made on a scanning SLM-AMINCO 4800 spectrofluorometer, which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter.

Nile Red-adsorbed TiO$_2$/Y zeolite or TiO$_2$/Y zeolite were directly mixed with 5.0$\times$10$^{-5}$ M aqueous Methyl Orange solution under argon gas flow. The mixture samples were split into Pyrex test tubes, and they were irradiated by using merry-go-round equipped with Xe-arc lamp attached with water filter and the cut-off filter transmitting the light longer than 320 nm. After a certain period of irradiation, each irradiated solution was filtered with 0.2 µm PVDF filter for removing Nile Red-adsorbed zeolite and its absorption spectra were measured to monitor the solution of Methyl Orange.

**RESULTS AND DISCUSSION**

Figure 1(a) shows the X-ray diffraction (XRD) pattern of TiO$_2$/Y zeolite was ion exchanged with aqueous solution of ammonium titanyl oxalate mono-hydrate, (NH$_4$)$_2$TiO(C$_2$O$_4$)$_2$H$_2$O. The XRD pattern of TiO$_2$/Y zeolite is well matched with that of HY zeolites. This indicates that the sample doesn’t contain an amorphous phase or TiO$_2$ phase and the framework structure of zeolite is unchanged during the ion exchange process. The titanium species residing in the zeolite cavities or channels are too small to be detected by XRD [10]. Infrared (IR) spectra of TiO$_2$/Y zeolites show new absorption bands at 920, 895, 860 cm$^{-1}$. According to Liu et al.’s report, the monomer Ti$-$O and Ti$-$O$-$Ti linkage vibrations have frequencies of 1087 and 975 cm$^{-1}$, respectively, and the Ti$-$N$-$Ti linkage vibration is around 850 cm$^{-1}$ [15]. This indicates that the TiO$_2^+$ species as well as Ti$-$O$-$Ti linkages are also present in the zeolites. In addition to the new bands at 920, 895, 860 cm$^{-1}$, the IR spectra also show a slight shift of the T$-$O$-$T or O$-$T$-$O (T = Si or Al) stretching vibration of the framework (around 1000 cm$^{-1}$) toward higher frequency, illustrating the effect of the Ti species on the zeolites framework. Calcination of the samples at 550°C causes overlapping of the new absorption bands in the IR spectra, and the fine structure of the bands is no longer observed. This implies that a further aggregation of the Ti species to form larger particles in the zeolites cavities takes place [10,15]. The TiO$_2$/Y zeolite shows a broad band around 908 cm$^{-1}$ (Figure 1b). This IR spectral band was matched for with that of
previous reports of the titanium-exchanged zeolites Y [13,15]. The TiO$_2$/Y zeolite exhibits different features in the IR spectrum of the HY zeolite. This phenomenon supports that the direct introduction of the Ti species into zeolites cavities through the ion-exchange procedures.

The diffuse reflectance absorption spectrum of Nile Red-adsorbed TiO$_2$/Y zeolite is shown in Figure 2(a) with the absorption spectrum of Nile Red in acetonitrile. The absorption spectrum of Nile Red is broad with its band maximum located at 630 nm in TiO$_2$/Y zeolite and at 535 nm in acetonitrile. The diffuse reflectance spectrum of Nile Red-adsorbed TiO$_2$/Y zeolite is a little red-shifted from the absorption maximum of Nile Red in acetonitrile. Figure 2(b) shows the emission spectra of Nile Red in acetonitrile and TiO$_2$/Y zeolite. The emission spectra reveal remarkable changes in the emission band position as a function of medium, as in the case of the absorption spectra. This is probably due to the molecules of Nile Red strongly sensitive to the polarity of their micro-environment. Similar results were observed for Na$^+$-exchanged Y zeolites [16]. Not only in the supercages of zeolite they can be characterized as superpolar (the supercages are much more polar than all organic solvents) but also in the organic solvent, respectively which agree with reported results; for example, the absorption band maximum shift from 488 nm in hexane to 565 nm in methanol and the corresponding emission shifts from 525 nm in hexane to 625 nm in methanol [17]. Such large shifts in the absorption and emission band maxima may be attributed to the large excited state dipole moment of the molecule in polar media.

Nile Red exhibits nearly complete charge separation between the diethylamino group which acts as an electron donor and quinoid part of the molecule which is the electron acceptor due to the rotation of the flexible diethylamino group attached to the rigid structure of the molecule [18-20] (Scheme 1). The charge separation may be explained by the formation of the twisted intramolecular charge transfer (TICT) of molecule in polar solvents. The excitation spectra of Nile Red monitored at the two emission maxima reveal two distinct peaks in methanol-water (binary mixture): the distinct differences between the band position provide that the bands originate from completely different species or configurational states, which is in agreement with the TICT model [18]. 4-$N,N'$-dimethylaminobenzonitrile(DMABN) is one of the TICT molecules which show dual fluorescence in polar solvents: a large Stokes’ shifted emission of the excited TICT state in addition to the normal emission from the local excited state. Unlike DMABA, Nile Red shows only single broad emission band in pure polar solvent (Figure 2b) by efficient energy transfer from the higher configurational energy state to the lower configurational energy state [18,19]. This indicates that Nile Red encapsulated within TiO$_2$/Y zeolite exist in TICT state in which wholly photoinduced charge separation occurs.

To confirm the superpolarity of supercages, we attempted to measure the fluorescence lifetime of the Nile Red-adsorbed TiO$_2$/Y zeolites. Figure 3 shows typical temporal profile of fluorescence decay for the Nile Red-adsorbed TiO$_2$/Y zeolite.

![Figure 2. (a) Absorption spectra and (b) Emission spectra of Nile Red in both acetonitrile (dotted line) and TiO$_2$/Y zeolite (solid line).](image)

![Scheme 1. Nile red structural formulas: (A) planar and (B) twisted.](image)

![Figure 3. The fluorescence decay profile of the normal emission of Nile Red-adsorbed TiO$_2$/Y zeolite monitored at 660 nm. The excitation wavelength is 580 nm.](image)
The transition of Nile Red from the excited singlet state to the fluorescence TICT state is so fast that the rise of the fluorescence intensity is not observed [18,21]. For the Nile Red-adsorbed TiO₂-Y zeolites, TICT emission decays with the two decay times (1.6 ns, 380 ps). The 1.6 ns decay component is attributed to the emission from stabilized TICT state while 380 ps component corresponds to the rotational reorientation time(τ_r). The one decay time (1.6 ns) is remarkable contrast to those for the TICT emission measured in various solutions. For example, the fluorescence lifetime of Nile Red is 3.6 ns in ethanol and 5.1 ns in CCl₄[21]. This indicates that fluorescence lifetime decreased with increase in the polarity of the medium. This comparison leads to the conclusion that the relatively short fluorescence lifetime of Nile Red in TiO₂/Y zeolites as compared to that in all organic solvents is attributable to the high polarity of zeolite cavities.

Unlike other TICT molecules, Nile Red in TiO₂/Y zeolite shows only single fluorescence corresponding to the TICT state of completely charge separation. This indicates that the photochemical electron transfer between Nile Red and TiO₂/Y zeolite could be progressed efficiently more than DMABA in TiO₂/Y zeolite. The photochemical interaction should be caused by an electron transfer from Nile Red to the conduction band of TiO₂ attached inside the nanopore frame of the zeolite. The photoinduced electron transfer from the exited singlet state of DMABA to TiO₂ conduction band has been previously observed from DMABA-adsorbed TiO₂/Y zeolites [13]. However, the photochemical interaction should be the electron transfer from the excited TICT state of Nile Red to TiO₂ conduction in this photocatalytic system of Nile Red-adsorbed TiO₂/Y zeolite. This could result in enhancement of electron transfer efficiency to the frame of TiO₂/Y zeolite, and the electron subsequently should be accessible for reduction of some other substrate outside the zeolite.

In order to confirm the above speculation, we attempted to observe the photocatalytic activities of the Nile Red-adsorbed TiO₂/Y zeolite by monitoring the photoreduction of Methyl Orange (5.0×10⁻³ M) in aqueous solution. Figure 4 shows the UV-vis spectra of Methyl Orange before and after irradiation (≥ 320 nm) in the presence of Nile Red-adsorbed TiO₂/Y zeolite. Methyl Orange itself in the absence of TiO₂/Y zeolite was photochemically inert as observed by no change in the absorption spectrum. Furthermore, methyl orange and Nile Red mixture was also photochemically inert. However, in the presence of Nile Red-adsorbed TiO₂/Y zeolite, the absorption spectrum of Methyl Orange was significantly changed (Figure 4). The visible absorption band of methyl orange disappears in at 460 nm and a new peak grows in at 247 nm, which was originated from photoreduction product, hydrazine derivative [22]. The spectral change of Methyl Orange solution was also observed by irradiating in the presence of free TiO₂/Y zeolite, but the bleaching is very weak. This indicates that light absorbed TiO₂ as well as Nile Red will lead to destruction of Methyl Orange. Furthermore, no absorption spectral shift was observed at 460 nm, indicating the Methyl Orange could be reduced by Nile Red-adsorbed TiO₂/Y zeolite and free TiO₂/Y zeolite. These results imply that the photoreduction of Methyl Orange is catalyzed by the TiO₂/Y zeolite. Figure 5 shows the degree of the bleaching of methyl orange as a function of irradiation time. This exhibits the photocatalytic activity of Nile Red-adsorbed TiO₂/Y zeolite about eight times higher than free TiO₂/Y zeolite, indicating that Nile Red-adsorbed on TiO₂/Y zeolite plays an important role in increasing the.

Figure 4. Absorption spectral change of the filtered solution of Methyl Orange after irradiation in the presence of Nile Red-adsorbed TiO₂/Y zeolites. Concentration of Methyl Orange was 5.0×10⁻³ M. The irradiation wavelength is longer than 320 nm. ‘T’ stand for the irradiation times (minutes).

Figure 5. Plot of the absorption change of Methyl Orange 460 nm as a function of irradiation time in the presence of Nile Red-adsorbed TiO₂/Y zeolite(○), and free TiO₂/Y zeolite(●).
The most available sunlight. Organic compounds because Nile Red absorb the visible light, would be very useful for the cleaning of wastewater containing and reused as the photocatalyst. Therefore, this photocatalyst electron density in conduction band of TiO₂ on the zeolite is Nile Red to TiO₂ on the TiO₂/Y zeolite. Consequently, the used to induce electron transfer from the excited TICT state of UV light, the conduction band electron can be removed quickly from the TiO₂ site before charge recombination, because the electron-rich zeolite surface function as a hole scavenger [23]. This is the reason why the free TiO₂/Y zeolite catalyzes the photoreduction of Methyl orange, even though the efficiency is low (<10%). However, in the Nile Red-adsorbed TiO₂/Y zeolite, Nile Red also absorbs visible light used to induce electron transfer from the excited TICT state of Nile Red to TiO₂ on the TiO₂/Y zeolite. Consequently, the electron density in conduction band of TiO₂ on the zeolite is increased as compared to the free TiO₂/Y zeolite. The excess conduction band electrons of TiO₂ on the zeolite frame could be transported through more efficiently than the case of free TiO₂/Y zeolite.

CONCLUSION

The Nile Red can be entrapped into the nanopores of TiO₂/Y zeolite, playing an important role in enhancement of electron density on the conduction photocatalytic activity of TiO₂/Y zeolite for the reduction of organic compounds in water. Furthermore, it should be also noted that the Nile Red-adsorbed TiO₂/Y zeolite could be successfully recovered by filtration and reused as the photocatalyst. Therefore, this photocatalyst would be very useful for the cleaning of wastewater containing organic compounds because Nile Red absorb the visible light, the most available sunlight.

REFERENCES


