TiO$_2$/Y-Zeolite encapsulating intramolecular charge transfer molecules: a new photocatalyst for photoreduction of methyl orange in aqueous medium

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Abstract

An intramolecular charge transfer (ICT) molecule, p-N,N$'$-dimethylaminobenzoic acid (DMABA) has been adsorbed onto nanoscale pores of TiO$_2$/Y-zeolite and its spectroscopic properties have been studied. The DMABA adsorbed on TiO$_2$/Y-zeolite shows dual emission band originated from the locally excited state and the ICT state. The ICT emission of DMABA in TiO$_2$/Y-zeolite is very weak as compared with that observed in homogeneous solution and other heterogeneous systems. This is attributed to an efficient electron donation from the excited singlet state of DMABA to the conduction band of TiO$_2$ on the zeolite. The conduction band electron of TiO$_2$ can be transported through the frame as demonstrated by the photocatalytic reduction of methyl orange dissolved in aqueous solution. The quantum efficiency of the photocatalytic reduction of methyl orange is about 34% using 320 nm light. The DMABA is little destroyed during the degradation of methyl orange. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

From the viewpoint of green chemistry, the photocatalytic decomposition of organic compounds in wastewater has attracted a great deal of attention [1–12]. The TiO$_2$ is one of the most effective photocatalysts because it is generally biologically and chemically inert and photostable with near-UV band gap energy. The fine TiO$_2$ powder or crystals can be dispersed in the water to be clarified by irradiation, but they should be removed by filtering after reaction, which is troublesome and costly. Thus, in order to solve this problem, many researchers have examined some methods for fixing TiO$_2$ on other supporting materials including glass beads [10–12], fiber glass [13–15], silica [16,17], an electrode [18], and zeolite [19,20]. Recently, some researchers have used zeolite as hosts to fix semiconductors because it has unique uniform pores and channel size. Since encapsulation of TiO$_2$ into zeolite was first introduced by Krueger et al. [21] and liu et al. [22,23], many more encapsulation methods [24–27] have been developed to produce small particle sizes exhibiting quantum size effects or some improved photochemical reactions. However, it still remains difficult to obtain high efficiency of the photodecomposition of organic substrate in water

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with respect to UV photons except by the photoelectrochemical method [28], and the cost to clear large volume of wastewater in short time is very high.

The aim of this work is to enhance both the photocatalytic and recovery efficiencies by combining Ti-ion exchanged HY zeolite (TiO$_2$/Y-zeolite) and an ICT molecule. An ICT molecule, *p-N,N'*-dimethylaminobenzoic acid (DMABA) has been investigated in NaY, CaY and HY zeolite [29] as well as in different heterogeneous media [30–32]. Through these studies we have found that the hydrogen bonding of the carboxylic acid group of the intramolecular charge transfer (ICT) molecule on the surface of the heterogeneous media plays an important role in the photoinduced ICT dynamics. Consequently, the ICT molecule-adsorbed TiO$_2$ colloids improved the efficiency of the electron transfer from the TiO$_2$ conduction band [33]. Thus, by restricting the ICT molecule into the TiO$_2$/Y-zeolite host, we anticipate creating a photocatalytic system that is highly efficient for both water purification and recovery capability.

2. Experimental

2.1. Materials

The titanium-exchanged zeolite were prepared by a method of ion exchange of HY zeolite with an aqueous solution of ammonium titanyl oxalate monohydrate, (NH$_4$)$_2$ TiO(C$_2$O$_4$)$_2$·H$_2$O (from Aldrich) aqueous solution [22,23]. The HY zeolite were prepared by ion exchanging with the NaY zeolite (Si/Al = 2.47, from Aldrich) with 0.1 M NH$_4$Cl. After rinsing the zeolite with the triply distilled water several times, calcination was carried out at 500°C for 15 h. The temperature of the sample was elevated with a rate of 3.3°C/min. The sample was cooled down by decreasing elevated temperature again with the same rate. The amount of the exchanged titanium cation in the zeolite was calculated by taking the amount of TiO$_2$ left in the supernatant liquid. The ion-exchanged zeolite has 7.2 Ti species each unit cell. The titanium-exchanged zeolite 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 calcined at 450–500°C for 8 h. The TiO$_2$/Y-zeolite were fully characterized by XRD and

IR spectroscopic measurements TiO$_2$/Y-zeolite were transferred to a Pyrex cell and activated at 200°C for 2 h under vacuum (10^{-5} Torr), then shaken with 25 ml degassed acetonitrile solution containing 1.0 mM of DMABA for 12–15 h. To remove acetonitrile, the solid was dried at 80°C for 18 h. The dried solid was transferred to quartz cell under the vacuum for the spectroscopic measurements.

2.2. 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 SINCO UVS 2040 spectrophotometer. 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.

The DMABA-adsorbed TiO$_2$/Y-zeolite or free TiO$_2$/Y-zeolite were directly mixed with 5.0×10^{-6} 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 DMABA-encapsulated zeolite and its absorption spectra were measured to monitor the solution of methyl orange.

3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) pattern of TiO$_2$/Y-zeolite prepared by the ion-exchanged method. The XRD pattern of TiO$_2$/Y-zeolite is well matched with that of the HY zeolite. This indicates that the framework structure of zeolite is unaltered during the ion-exchange process. The titanium species residing in the zeolite cavities or channels are too small to be detected by XRD [10]. To certify the entrapped titanium in zeolite, its IR spectra are recorded,
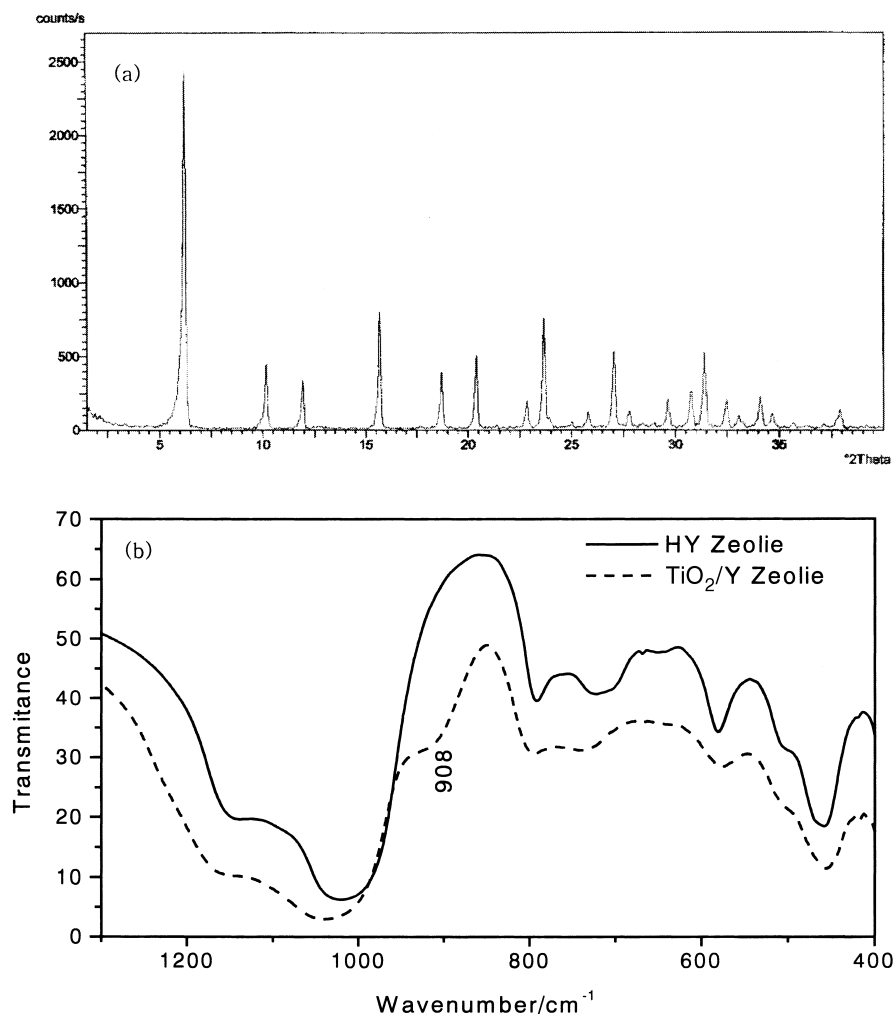
Fig. 1. (a) The X-ray diffraction pattern of TiO$_2$/Y-zeolite and (b) the IR spectra of HY and TiO$_2$/Y-zeolite.

and three absorption bands at 920, 895 and 860 cm^{-1} are observed. According to the Liu et al. [23], these three absorption bands are originated from the Ti–O and Ti=O stretching vibration and Ti–O–Ti linkage vibration, respectively [23,34]. Thus, those IR data reflect that the TiO^{2+} species, and titanium in the form of Ti–O–Ti are incorporated into the zeolite [23]. In addition to that, the spectra also show a slight shift of the T–O–T or O–T–O (T = Si or Al) stretching vibrations of the framework (around 1000 cm^{-1}), and illustrate the effect of the Ti species on the zeolite framework. Calcination of the samples at 550°C causes overlapping of the 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 in zeolite cavities may occur, and the TiO$_2$/Y-zeolite shows the broad band around 908 cm^{-1} (Fig. 1b) [22,23].

Fig. 2a shows the diffuse reflectance absorption spectrum of TiO$_2$/Y-zeolite, and its band gab energy (3.4 eV) is quite similar to that of the TiO$_2$ colloidal solutions, indicating the optical properties of colloidal TiO$_2$ and entrapped Ti species are the same [22]. Fig. 2b and c shows the diffuse reflectance absorption and fluorescence emission spectra of DMABA adsorbed on TiO$_2$/Y-zeolite. The absorption spectrum is
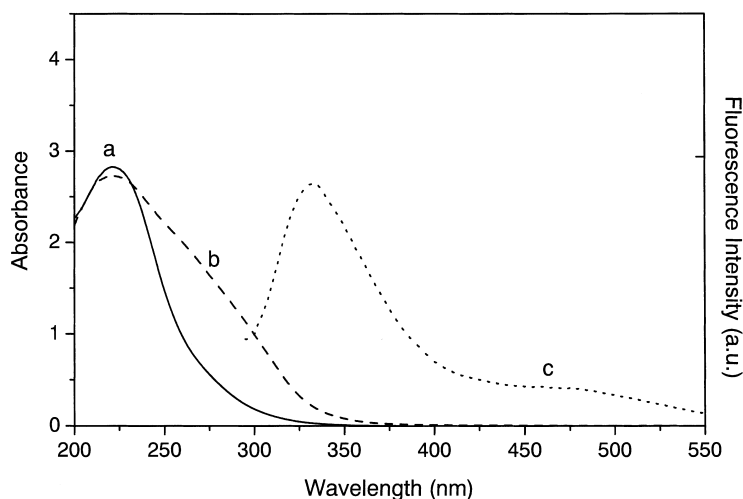
Fig. 2. Diffuse reflectance absorption of free TiO$_2$/Y-zeolite (a), the DMABA-adsorbed TiO$_2$/Y-zeolite (b), and fluorescence emission spectra of DMABA-adsorbed TiO$_2$/Y-zeolite (c).

nearly the same as that observed for DMABA encapsulated in NaY zeolite [29], indicating that a single molecule of DMABA is homogeneously entrapped in the surpercage of the TiO$_2$/Y-zeolite. This encapsulation can be also certified by the Xe-NMR experiments [29]. The fluorescence spectrum exhibits dual emission bands as observed from DMABA in acetonitrile solution [33] or NaY zeolite [29], and the emission at shorter wavelength (340 nm) is originated from the locally excited state while the other emission at 480 nm is originated from the excited ICT state. The ratio of ICT emission to the local emission (ICT/LE) is quite small as compared with that of DMABA in polar zeolite cavity [29] or SiO$_2$ colloidal solution [33] and even acetonitrile solution [33,35], implying a certain photochemical interaction between DMABA and TiO$_2$/Y-zeolite [29]. The photochemical interaction should be an electron transfer from DMABA to the conduction band of TiO$_2$ attached inside the nanopore frame of the zeolite. Being consistent with this, the photoinduced electron transfer from the locally excited singlet state of DMABA to TiO$_2$ conduction band has been previously observed from the DMABA-adsorbed TiO$_2$ colloidal solution system [36]. This could result in enhancement of electron transfer efficiency to the frame of TiO$_2$/Y-zeolite, and the electron subsequently should be accessible for reduction of some other substrate outside the zeolite.

In order to confirm the speculation above, we attempted to observe the photocatalytic activities of the DMABA-adsorbed TiO$_2$/Y-zeolite by monitoring the photoreduction of methyl orange (5.0×10^{-6} M) in aqueous solution. Fig. 3 shows the UV–VIS spectra of methyl orange before and after irradiation (≥ 320 nm) in the presence of TiO$_2$/Y-zeolite. Methyl orange itself in the absence of TiO$_2$/Y-zeolite was photochemically inert as observed by no change in the absorption spectrum. Furthermore, methyl orange and DMABA mixture was also photochemically inert. However, in the presence of DMABA-adsorbed TiO$_2$/Y-zeolite, the absorption spectrum of methyl orange was significantly changed (Fig. 3a). The visible absorption band decreases and a new peak grows in at ca. 250 nm, which was originated from reduction product, hydrazine [37]. The spectral change of methyl orange solution was also observed by irradiating in the presence of free TiO$_2$/Y-zeolite, but the bleaching is very weak. Furthermore, no absorption spectral shift was observed at 470 nm, indicating the methyl orange could be reduced by DMABA adsorbed TiO$_2$/Y-zeolite and free TiO$_2$/Y-zeolite. These results imply that the photoreduction of methyl orange is catalyzed by the TiO$_2$/Y-zeolite. Fig. 4 shows the degree of the bleaching of methyl orange as a function of irradiation time. This exhibits the photocatalytic activity of DMABA-adsorbed TiO$_2$/Y-zeolite six times
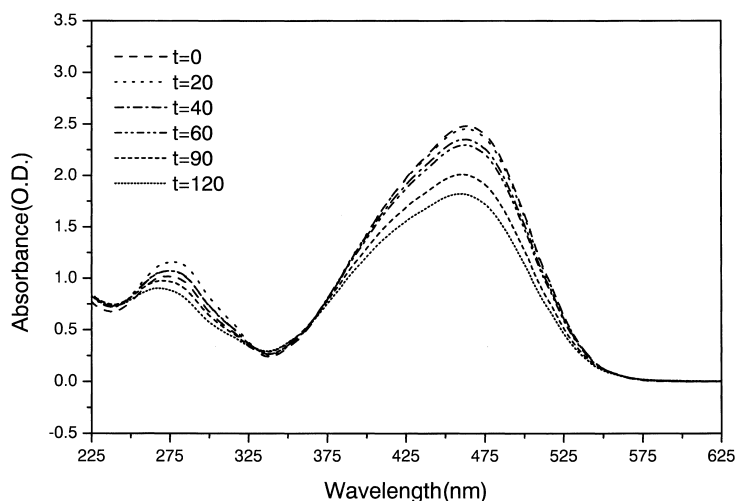
Fig. 3. Absorption spectral changes of the filtered solution of methyl orange after irradiation in the presence of DMABA-adsorbed TiO$_2$/Y-zeolite. Concentration of methyl orange was 5.0×10^{-6} M. The irradiation wavelength is longer than 320 nm.

higher than that of free TiO$_2$/Y-zeolite, indicating that DMABA adsorbed on TiO$_2$/Y-zeolite plays an important role in increasing the photocatalytic activity of TiO$_2$/Y-zeolite.

The reduction of methyl orange is shown in Scheme 1 involving accepting electron transport through the TiO$_2$/Y-zeolite frame.

Upon irradiation of TiO$_2$ on TiO$_2$/Y-zeolite by UV-light (band gap energy: 3.4 eV), the conduction band electron can be removed quickly from the TiO$_2$ site before charge recombination, because the electron-rich zeolite surface functions as a hole scavenger [24,27,28]. This is the reason why the free TiO$_2$/Y-zeolite catalyzes the photoreduction of methyl orange, even though the efficiency is low (<10%). However, in the DMABA-adsorbed TiO$_2$/Y-zeolite, DMABA also absorbs UV-light used to induce electron transfer from the excited singlet state of DMABA
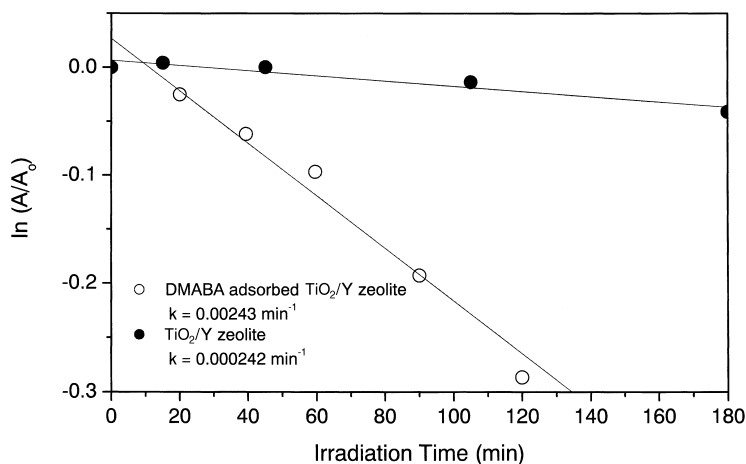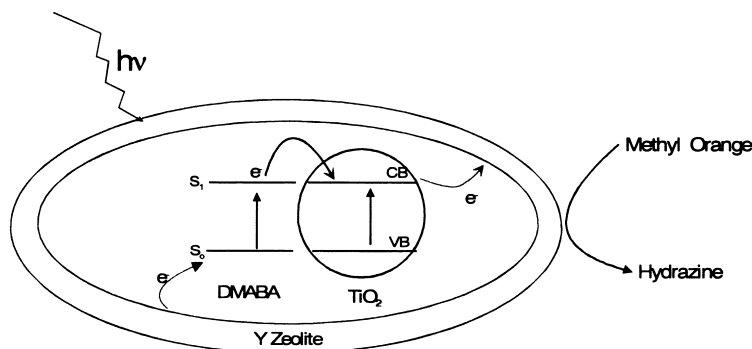

Fig. 4. Plot of the absorption change of methyl orange at 470 nm as a function of irradiation time in the presence of DMABA-adsorbed TiO$_2$/Y-zeolite (○), and free TiO$_2$/Y-zeolite (●).

Scheme 1.

to TiO_2 on the TiO_2/Y-zeolite. This is consistent with the observation of electron transfer from DMABA to NaY zeolite [29]. Consequently, the electron density in conduction band of TiO_2 on zeolite is increased as compared to free TiO_2/Y-zeolite. The excess conduction band electrons of TiO_2 on the zeolite frame could be transported through more efficiently than the case of free TiO_2/Y-zeolite. Thus, the quantum efficiency of the photocatalytic reduction of methyl orange is about 34% with using 320 nm light.

4. Conclusion

The DMABA can be entrapped into the nanopores of TiO_2/Y-zeolite, playing an important role in enhancement of electron density on the conduction band of TiO_2 on the zeolite frame to enhance the photocatalytic activity of TiO_2/Y-zeolite for the reduction of organic compounds in water. Furthermore, it should be also noted that the DMABA-adsorbed TiO_2/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 using UV-light.

Acknowledgements

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