Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 77 (2008) 327–334

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Photocatalytic discolorization of methyl orange solution by Pt modified TiO_2 loaded on natural zeolite

Miaoliang Huang*, Chunfang Xu, Zibao Wu, Yunfang Huang, Jianming Lin, Jihuai Wu

Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou, Fujian 362021, China

Received 10 October 2006; accepted 17 January 2007
Available online 9 June 2007

Abstract

Pt modified TiO_2 loaded on natural zeolites (Pt–TiO_2/zeolites) was prepared by sol–gel technique and photoreductive deposition method. The photocatalysts were characterized by UV–vis absorption spectrum, FTIR spectrum, BET and X-ray diffraction. Their photocatalytic activities were examined by the photocatalytic decolorization of methyl orange solution under UV light irradiation. The results show that Pt doping induced the enhancement of photocatalytic decolorization and optimal Pt doping is about 1.5 wt.% with 86.2% of decolorization rate under 30 min irradiation time. The effects of calcinated temperature, catalyst concentration, oxidant H_2O_2, and pH on the photocatalytic activities were studied. The repeatability of photocatalytic activity was also tested and the decolorization rate was 81.9% of initial decolorization rate after five cycles.

Keywords: Natural zeolite; TiO_2; Pt doping; Methyl orange; Photocatalysis

1. Introduction

Heterogeneous photocatalysis based on TiO_2, as a new ‘‘advanced oxidation processes’’, has attracted much attention because of its application in the eliminations of aqueous and gaseous pollutants [1–7]. Compared with other semiconducting materials, TiO_2 has been studied extensively due to its high photocatalytic activity, non-toxicity, low cost and chemical stability. There are two commonly used types for TiO_2 photocatalyst in experimental investigation and practical application: suspended TiO_2 particles and supported TiO_2. In order to overcome the trouble of the separation for superfine TiO_2 particles after reaction, the main attempts are focused on the research of immobilizing TiO_2 on supports, including stainless steel [8], activated carbon [9], fiber glass [10], clay [11], zeolite [12], etc. Zeolite seems to be a promising support for TiO_2 photocatalyst because of its regular pores and channel sizes, and good adsorption ability. TiO_2 supported on zeolite integrates the photocatalytic activity of TiO_2 with the adsorption properties of zeolite together, which induce a synergistic effect, resulting in the enhancement of photocatalytic efficiency. Some investigation results indicate that zeolites, including synthetic zeolites such as HZSM-5, ZSM-5, 13X, 4A, β, HY, Hβ, USY, Y zeolites as well as molecular sieve (MCM-41), are effective supports for TiO_2 photocatalyst [12–22]. In recent years, the natural mineral materials, such as a natural pumice [23], natural zeolite [24], have also attracted an increasing interest due to their layered or porous structure, low cost and abundant storage. In our previous work, we have also reported the photocatalysts of TiO_2 immobilized on the natural zeolite by sol–gel process, and investigated the effects of the amount of TiO_2 loading and the catalysts concentration on the photocatalytic activities by using methyl orange as a model compound [25].

Earlier studies have revealed that the photocatalytic activity of TiO_2 can be improved significantly by doping with noble metals such as Pt, Au, Ag, etc. [26–32], which has been explained by the action of noble metal as photogenerated

---

* Corresponding author.
E-mail address: huangml@hqu.edu.cn (M. Huang).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.01.026

electron acceptor. Under UV light irradiation, the photogenerated electrons quickly transfer from TiO_2 surfaces to the Pt particles, leading to electron–hole effective separation and resulting in the improvement of photocatalytic efficiency [31]. To continue our previous work [25], this work is aim at investigating the photocatalytic activity of Pt modified TiO_2 loaded on the natural zeolite by using methyl orange as a target degraded compound; methyl orange is a kind of azo dyes and has been used as a probe for photocatalytic decolorization [29,33–36], the degradation process of which has been analyzed by Baiocchi et al. [33]. The effects of added H_2O_2, pH in solution, and amount of doped Pt on the photocatalytic activity, and the repeatability of the photocatalytic activity is also performed in this study.

2. Experiment

2.1. Chemicals

Natural zeolite was a gift from Jinyun Shenshi Kaifa company, Zhejiang province. Its main components consist of SiO_2 (70.45%), Al_2O_3 (12.35%), MgO (1.68%), K_2O (1.14%), Fe_2O_3 (0.59%), MnO (0.05%), Na_2O (1.09%), CaO (1.66%) and other materials including water (10.99%). Tetra-*n*-butyl titanate and *n*-butyl alcohol were purchased from Shanghai Chemical Reagent Company, China. Chloroplatinic acid and nitric acid were obtained from Shantou Xilong Chemical Factory, Guangdong Province, China. Methyl orange was obtained from Beijing Chemical Reagent Company, China.

2.2. Preparation of photocatalyst

Pt modified TiO_2 loaded on natural zeolite was prepared by sol–gel process and photoreductive deposition method. The precursor solution composites consist tetra-*n*-butyl titanate, *n*-butyl alcohol, chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) and nitric acid. The nitric acid was used as catalyst to control the hydrolysis process. The typical steps are as follows:

(1) A given amount of tetrabutyl titanate was dissolved in pure ethanol with a volume ratio of 1:3 of tetrabutyl titanate to ethanol, and then nitric acid solution was added dropwise into the solution to readjust the pH value to 4. During these procedures, the solution was stirred vigorously to avoid precipitate. After stirring for 8 h, weak yellow and clear TiO_2 sol was obtained. Subsequently, requisite amount of natural zeolite, which was preheated at 450 °C for 4 h, was mixed with the TiO_2 sol with vigorous stirring, and a mixed suspension formed. After being stirred for 6 h, the mixture solution of ethanol and distilled water was added gradually into the mixed suspension, the mixed suspension became gel, then dried at 80 °C for 6 h, ground to fine powder in an agate mortar, and moved to oven to be further calcined at different temperatures (110 °C, 200 °C, 300 °C, and 500 °C) for 4 h. By this procedure, TiO_2 loaded on natural zeolite was prepared, denoted as TiO_2/zeolite.

(2) Pt modified TiO_2/zeolite was prepared by a photochemical reduction process [26]: certain amount of chloroplatinic acid was dissolved in the mixture solution of distilled water and methanol, and then a weighted amount of TiO_2/zeolite was put into the solution. The mixture solution was irradiated by UV light for 5 h, followed by washing and drying at 80 °C for 6 h. Pt modified TiO_2/zeolite composite was achieved, denoted as Pt–TiO_2/zeolite. Our previous investigation has revealed that the decolorization rate increased with the amount of TiO_2 loading and then decreased with further increase of TiO_2 loading. The decolorization rate was about 66.9% with 25% TiO_2 loading heated at 200 °C at 30 min irradiation time [25]. For a convenient comparison, in this experiment, the photocatalyst with 25% TiO_2 loading was used throughout experiments. Six final samples of Pt–TiO_2/zeolite with different Pt contents of Pt to TiO_2 (0, 0.5, 1.0, 1.5, 2.0, 3.0 wt.%) were prepared.

2.3. Characterization of photocatalyst

The XRD patterns of prepared samples were recorded by Bruker D8 Advance X-ray diffractometer with Cu Kα irradiation (operating at 40 KV and 30 mA, $\lambda = 0.154059$ nm). The FTIR spectra were performed on the Nicolet Nexus-470 FTIR spectrometer. The absorption spectra were measured by using a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer equipped with an integrating sphere. The Morphology of sample was observed by Hitachi S-3500N scanning electron microscope and elemental analysis was performed with energy dispersive X-ray (EDX) spectroscopy (Oxford Inca). The Specific surface area was measured by N_2 adsorption at low temperature on Micromeritics ASAP 2010 apparatus.

2.4. Evaluation of photocatalytic activity

The photocatalytic activity of the catalyst was evaluated by the photodecolorization of methyl orange (MO) solution. The photocatalytic experiment was performed in a cylindrical reactor. A 500 W U-shape high-pressure mercury lamp with maximal emission at 365 nm was used as UV light source, located in a cylindrical center, the reactor was cooled by a cooling jacket to keep the chamber temperature at 298 K. The methyl orange was used as a target decolorized matter. A 200 ml methyl orange solution mixed with a certain amount of catalyst was injected into the reactor chamber and stirred continuously. A 15 ml mixture solution was taken from the chamber at a regular interval under UV light irradiation, followed by centrifugation and filtration, finally clear solution was obtained. Its absorption spectrum was analyzed by Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer (Japan). The decolorization rate of methyl orange was calculated by the following equation [13]:

$$\eta = \frac{C_0 - C}{C_0} = \frac{A_0 - A}{A_0} \times 100\% \qquad (1)$$

where C_0 and A_0 are the initial concentration and absorbency of methyl orange solution at 462 nm corresponding to maximum absorption wavelength; C and A are the concentration and absorbency of methyl orange solution at 462 nm after UV light irradiation at any time.

3. Result and discussion

3.1. XRD and EDX analyses

The XRD patterns of samples are illustrated in the Fig. 1. For comparison, the XRD pattern of the pure natural zeolite is also shown in Fig. 1, which is similar to that reported in Refs. [37–39]. The results reveal that the natural zeolite used in the experiment is mostly mordenite. At lower calcinated temperature, TiO_2 existed in the form of amorphous and few anatase phases. Comparing the XRD pattern of the pure natural zeolite, the intensities of some diffraction peaks of Pt–TiO_2/zeolite decrease or disappear, which is due to that the surface of zeolite is covered by amorphous or crystallized TiO_2. The characteristic peak of anatase TiO_2 corresponding to $2\theta \approx 25.4°$ ($d = 0.346$ nm) become stronger and sharper gradually with increase of calcinated temperature. It can be seen that the main peak positions of natural zeolite are unchanged, indicating that the structure of natural zeolite has a good thermal stabilization, and also revealing that most parts of TiO_2 are distributed on the surface of natural zeolite while the part of TiO_2 encapsulated into the cavities of natural zeolite. The diffractive peak of Pt is not found obviously due to the low doping.

Fig. 2(a) shows the SEM micrograph of Pt–TiO_2/zeolite. It can be seen that the sample has a size smaller than 10 μm. The analysis of Pt element was performed by energy dispersive spectroscopy in microarea, shown in Fig. 2(b). It is observed clear that Pt particles have been dispersed on the sample.

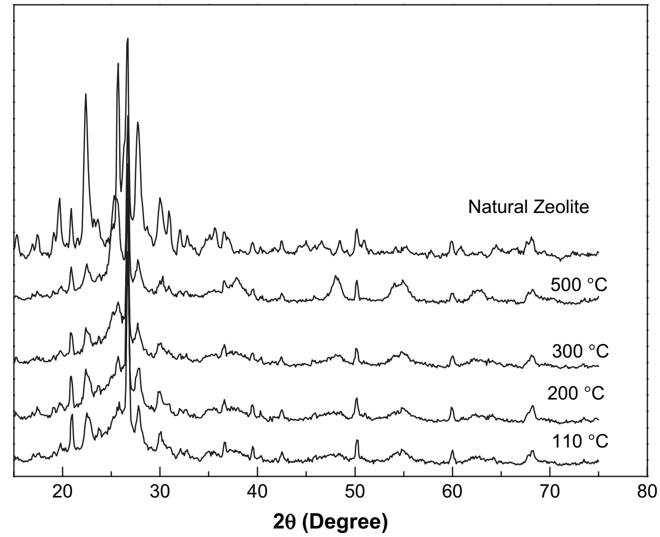

Fig. 1. XRD patterns of 1.5 wt.% Pt–TiO_2/zeolite at different calcinated temperatures.

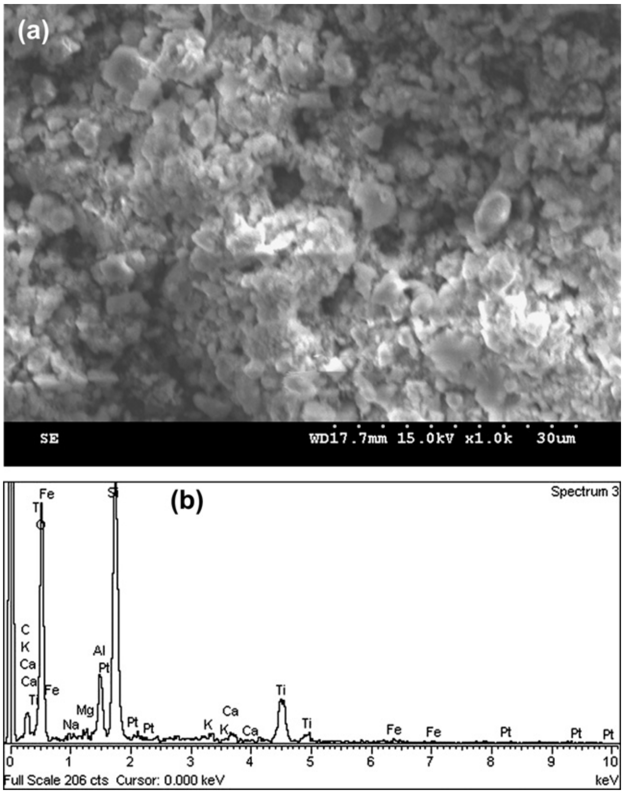

Fig. 2. Morphologies of Pt–TiO_2/zeolite (a) and the Pt element analysis (b).

3.2. FTIR analysis

Fig. 3 shows the FTIR spectra of natural zeolite and Pt–TiO_2/zeolite samples heated at different temperature. The region at 3150–3700 cm^{-1} is attributed to the hydroxyl stretching region of zeolitic water, its intensity decreases with increasing heating temperature due to the dehydrate in zeolite. The strongest absorption peak at 1047 cm^{-1} is assigned to

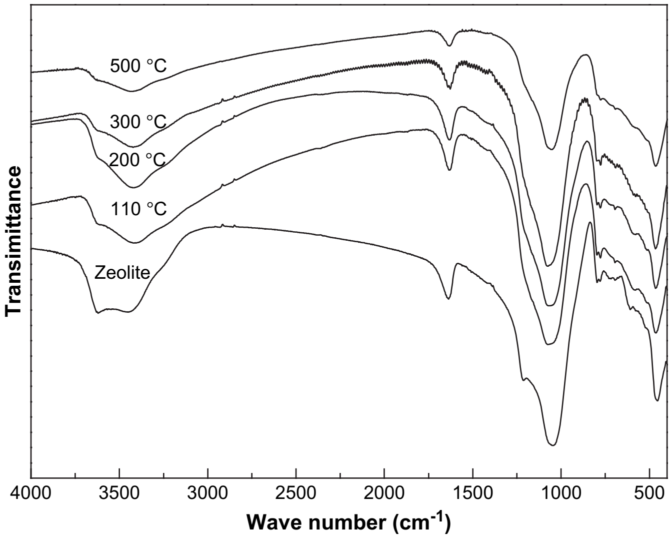

Fig. 3. FTIR spectra of 1.5 wt.% Pt–TiO_2/zeolite at different calcinated temperatures.

the framework stretching vibration band of Si(Al)–O in tetrahedral $Si(Al)O_4$ in natural zeolite, its position is unchanged at 500 °C treatment temperature, indicating that zeolite structure is not destroyed at 500 °C. The structural bands at 450–900 cm^{-1} are responsible for the stretching vibrations of T–O, T–O–T, and O–T–O bonds in tetrahedral SiO_4 and AlO_4. The band at 1630 cm^{-1} is attributed to the distorted OH group vibration in natural zeolite [37–39].

But no obvious band was observed at the region of 950–960 cm^{-1} assigned to the antisymmetric stretching vibration of Ti–O–Si bond [16]. It is suggested that no strong chemical interaction took place between TiO_2 and zeolite, hence TiO_2 maybe only disperse on the surface of zeolite, or encapsulate partly the zeolite cavity, the detailed results should be further examined.

3.3. *Photocatalytic decolorization experiment*

3.3.1. *Dark adsorption experiment*

Prior to photocatalytic experiment, the methyl orange adsorption in the dark on the photocatalysts of TiO_2/zeolite and Pt–TiO_2/zeolite was measured in the suspension. A 200 ml, 20 mg/l methyl orange solution was mixed with 0.4 g photocatalyst. The suspension was stirred magnetically for 2 h and reached the adsorption equilibrium. Then, 15 ml suspension was taken out from the reaction chamber, followed by several centrifugations to remove the catalyst and clear solution was obtained. Finally, its absorbency was measured by spectrophotometer, the results are listed in Table 1. It can be seen that the adsorption capacities of catalysts have only small difference.

3.3.2. *Effect of calcinated temperature*

Table 2 lists the relation between calcinated temperature and decolorization rate with 2 g/l of photocatalyst and 20 mg/l of methyl orange solution irradiated by UV light for 30 min and pH 6.2. For comparison, the result for Pt undoped sample was also given. From Table 2, it can be seen obviously that the decolorization rate is improved significantly by doping Pt, increases from 73% to 87.8% at 110 °C and from 66.9% to 86.2% at 200 °C for Pt undoped and 1.5 wt.% Pt doped catalysts, respectively. The decolorization rate decreases slightly from 87.8% to 86.2% with increase of the calcinated temperature from 110 °C to 200 °C for 1.5 wt.% Pt doped catalyst, and then decreases quickly with further increase of the calcinated temperature for Pt–TiO_2/zeolite. The decolorization rate shows a decrease tendency with increasing calcinated temperature for doped and undoped samples. Although increasing the calcinated temperature will accelerate the formation of TiO_2 anatase phase which is beneficial to the improvement of photocatalytic efficiency, it will also cause the conglomeration of catalyst particles, which reduces the specific surface areas of samples, resulting in the decrease of photocatalytic efficiency, hence catalyst calcined at lower temperature has a higher photocatalytic activity.

Table 1
The adsorption capacity for methyl orange on the photocatalysts calcinated at 200 °C with different Pt dopant percentages at pH = 6.2

Pt doping (wt.%)	0	0.5	1.0	1.5	2.0	3.0
Adsorption (%)	3.8	4.1	4.5	3.9	3.8	3.5

Table 2
The dependence of the decolorization rate and specific surface area of samples on the calcinated temperature

Temperature (°C)	TiO_2/zeolite		1.5% Pt–TiO_2/zeolite	
	Decolorization rate (%)	Specific surface area (m^2/g)	Decolorization rate (%)	Specific surface area (m^2/g)
110	73.0	107.2	87.8	118.7
200	66.9	78.5	86.2	86.1
300	58	63.2	66.9	57.8
500	31	25.2	43.2	34.8

Fig. 4 shows the relation between methyl orange solution concentration and irradiation time for the two samples of TiO_2/zeolite and 1.5 wt% Pt–TiO_2/zeolite with 20 mg/l of MO solution, pH = 6.2 and 2 g/l of catalyst dosage. It can be seen that the decolorization rate increases with irradiation time. The result shows that the photocatalytic activities of catalysts are improved by doping Pt.

For a convenient comparison, the samples of Pt–TiO_2/zeolites calcinated at 200 °C were used in the following experiments.

3.3.3. *Effect of catalyst concentration*

The effect of catalyst concentration on decolorization rate was studied by varying catalyst concentration from 0.5 g/l to 6 g/l. The results are illustrated in Fig. 5. It is found that the decolorization rate of methyl orange solution increased significantly from 59.2% to 90.5% with increase of catalyst concentration at a range from 0.5 g/l to 3 g/l and then decreased with

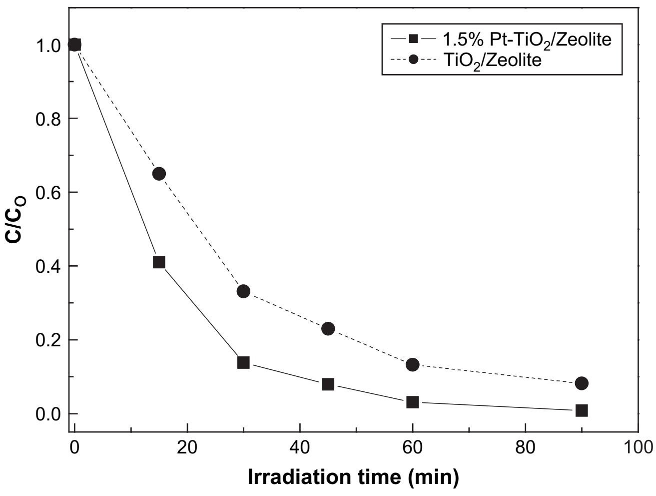

Fig. 4. The relation between methyl orange solution concentration and irradiation time for the two samples of TiO_2/zeolite and 1.5 wt% Pt–TiO_2/zeolite with 20 mg/l of MO solution, pH = 6.2 and 2 g/l of catalyst dosage.

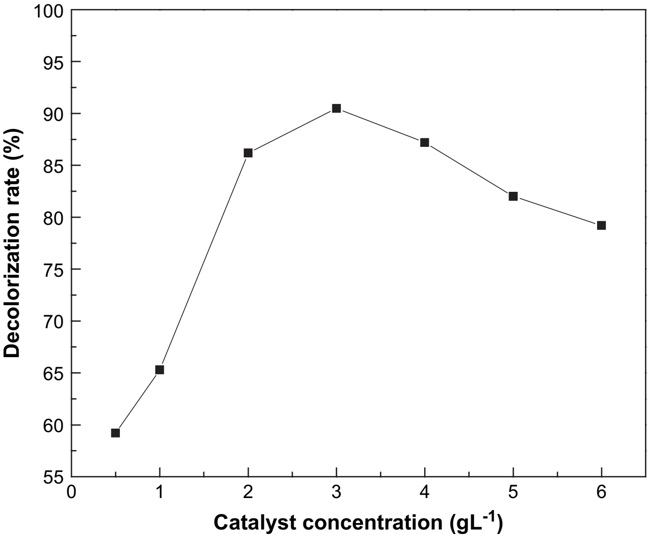

Fig. 5. Effect of catalyst concentration on decolorization rate of methyl orange solution. Catalyst: 1.5 wt.% Pt–TiO_2/zeolite; MO concentration: 20 mg/l; pH 6.2.

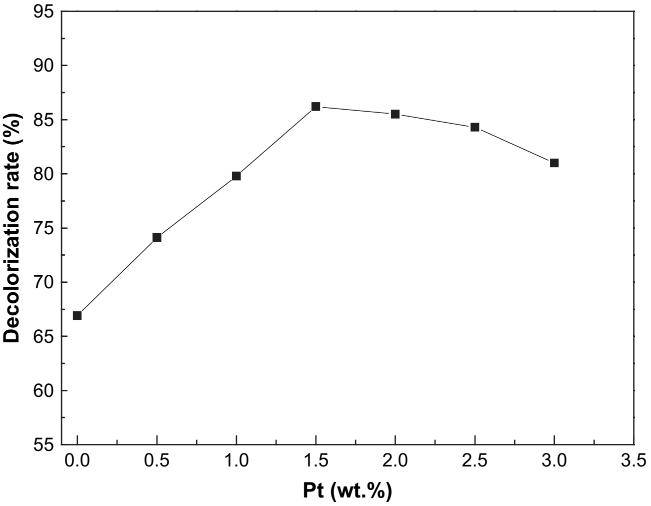

Fig. 6. The relation between the amount of doped Pt and the decolorization rate of methyl orange solution. Catalyst: 1.5 wt.% Pt–TiO_2/zeolite; dosage: 2 g/l; MO concentration: 20 mg/l; pH 6.2; irradiation time 30 min.

further increase of the catalyst concentration due to light scattering and screening effect, therefore, there exists an optimum concentration for a given substrate concentration. These phenomena were also observed in other experiments for the photodegradation of organic materials by TiO_2 powder or supported TiO_2 in aqueous solution and the detailed explanations have been given in Refs. [16,17]. It is suggested that at a lower level of catalyst concentration, increasing catalyst will provide more reactive sites resulting in the enhancement of the decolorization rate. At a higher level of catalyst concentration, although the reactive sites increases, the solution became cloudy and opaque, which reduce the light penetration and lead to the reduction of the availability of active site, while the increase of concentration maybe result in the agglomeration of the catalyst particles, hence the part of the catalyst surface became unavailable for photon absorption and dye adsorption, the decolorization rate subsequently decreases.

In this experimental reaction system, the optimum concentration of catalyst is about 3 g/l for a given concentration of 20 mg/l of methyl orange solution. From a practical application point of view, the concentration of 2 g/l is moderate.

3.3.4. Effect of Pt doping

The relation between the amount of doped Pt and decolorization rate is shown in Fig. 6. It is observed that the decolorization rate increases with the increase of the amount of doped Pt, reaches the maximum at 1.5 wt.% of the amount of doped Pt, and then decrease with further increase of the amount of doped Pt. Pt acts as an electron traps, the electrons generated on the TiO_2 surface by UV light illumination quickly move to Pt particle surface to facilitate the effective separation of the photogenerated electron and holes, resulting in the significant enhancement of photocatalytic activity [31]. At lower doping level, Pt plays a positive role as electron acceptor, more acceptor centers are provided with increasing Pt doping, therefore the decolorization rate for methyl orange increases with the increase of Pt doping. But excessive doping will also induce the conglomeration of Pt particles, which become the recombination center of photogenerated electron and hole, leading to the decrease of photocatalytic efficiency. Suitable Pt doping will enhance the photocatalytic efficiency. In this reaction system, 1.5 wt.% Pt doping is moderate.

3.3.5. Effect of added H_2O_2

The effect of added H_2O_2 on the decolorization of methyl orange was performed at a range of 0.4–2 mM/l of added H_2O_2 concentration, the results are illustrated in Fig. 7. The decolorization rate increases with increase of H_2O_2 concentration from 0.4 to 2 mM/l, and the maximum appears at 1.2 mM/l, and then decreases with increase of H_2O_2 concentration. The optimum concentration of adding H_2O_2 is about 1.2 mM/l. In photocatalytic degradation process, addition of adequate H_2O_2 is beneficial to the formation of hydroxyl radicals by following chemical reactions [40–42].

$$H_2O_2 + e^- \rightarrow OH^- + \bullet OH \tag{1}$$

$$H_2O_2 + \bullet O_2^- \rightarrow O_2 + OH^- + \bullet OH \tag{2}$$

$$H_2O_2 + h\nu \rightarrow 2\bullet OH \tag{3}$$

The hydroxyl radicals ($\bullet$OH) is a super strong oxidization and a dominant species in photocatalytic process, and able to oxidize a variety of organic substances completely on the surface of TiO_2 irradiated by UV light. Therefore, added H_2O_2 will facilitate the generation of $\bullet$OH and promote the photodegradation efficiency. However, under the condition of exorbitant H_2O_2 concentration, following reaction will occur in Eqs. (4)–(6),

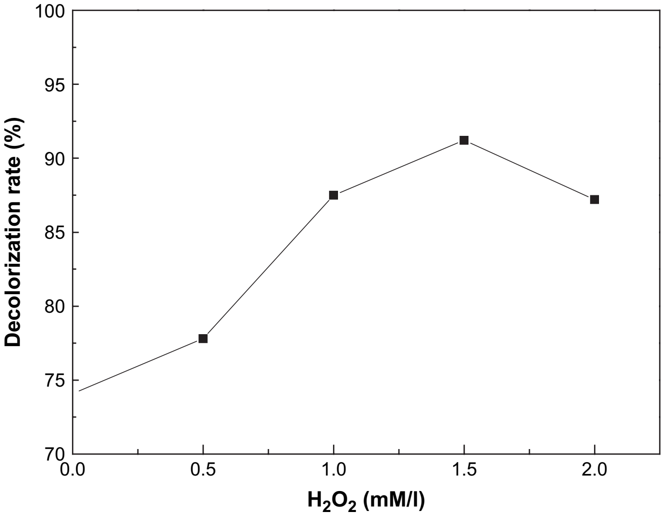

Fig. 7. Effect of addition of H_2O_2 on the decolorization rate of methyl orange solution. Catalyst: 0.5 wt.% Pt–TiO_2/zeolite; dosage: 2 g/l; MO concentration: 20 mg/l; pH 6.2; irradiation time: 30 min.

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet \quad (4)$$

$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \quad (5)$$

$$H_2O_2 + 2h^+ \rightarrow O_2 + 2H^+ \quad (6)$$

H_2O_2 acts as a scavenger of •OH and exhaust •OH in solution [40–42], and the decolorization reaction will be retarded, therefore, only moderate added H_2O_2 is beneficial to achieve higher degradation rate.

3.3.6. *Effect of pH*

In order to realize the effect of pH on the photocatalytic decolorization of methyl orange by Pt–TiO_2/zeolite, the experiment of the photocatalytic decolorization for methyl orange on the catalyst was performed at different pH values. The results are presented in Fig. 8. It can be seen that the decolorization rates of methyl orange are 98%, 86.2%, and 11.2% at pH 2.5, 6.2 and 11, respectively. The effect of pH on the decolorization rate is remarkable in our experimental condition. The decolorization rate in acidic condition is higher than that in alkaline condition. The similar effect trends of pH were observed in the photodegradation of methyl orange in other reaction systems [29,35,36].

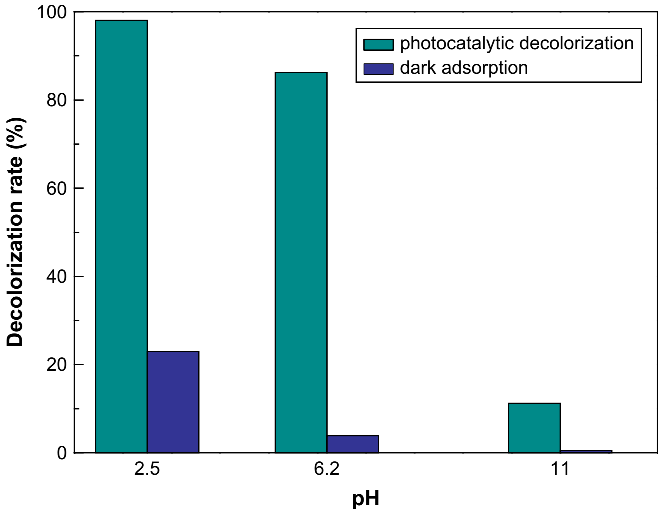

Fig. 8. Effect of pH on the decolorization rate of methyl orange solution. Catalyst: 1.5 wt.% Pt–TiO_2/zeolite; dosage: 2 g/l; MO concentration: 20 mg/l; irradiation time: 30 min.

It was difficult to elucidate clearly the mechanism of the effect of pH on photocatalytic process. In general, pH change will affect the surface properties of catalyst, such as surface charged properties and the absorption behavior for target organic materials. The zero point charge (zpc) pH_{zpc} for TiO_2 is at about 6.8 [16]. At lower or higher than pH_{zpc}, TiO_2 is positively charged or negatively charged, therefore in acidic condition, the positively charged TiO_2 surface is available for the absorption of negatively charged methyl orange facilitating the degradation reaction, and high photocatalytic efficiency is obtained. On the contrary, in alkaline condition, the absorption of methyl orange on TiO_2 surface decreases because of the coulumbic repulsion between the negative catalyst surface and dye anions resulting in the decrease of photocatalytic decolorization rate. It was verified in our experiment by performing the dark absorption of the methyl orange on the catalyst, the dark absorption rates are 23%, and 3.9% at pH 6.2, only 0.51% at pH 11, respectively. It can be seen clearly that the dark decolorization of methyl orange is much higher in lower pH than in higher pH, indicating that the strong adsorption of methyl orange on the catalyst plays a positive role to enhance the decolorization rate in the acidic condition. At high pH values, although the hydroxyl radicals can be formed through OH^- reaction with photogenerated holes, the hydroxyl radicals are rapidly scavenged and they do not have the opportunity to react with dyes, as well as there is a weak adsorption, resulting in the reduction of photocatalytic decolorization rate [40], therefore the decolorization rate is quite small, only 11.2% at in this experiment.

However, some different trends of pH effect were obtained. Sakthivel et al. found that the optimal degradation rate did not occurred in the maximum adsorption of dye on ZnO in the photocatalytic degradation of azo dye acid brown 14 by ZnO [43], and Muruganandham and Swaminathan [44] reported that the effect of dye adsorption on photocatalytic activity is limited and may not be the only determinative factor for the photocatalytic degradation in the photocatalytic degradation of Reactive Orange 4 by TiO_2–UV process.

It should be noted that the surface properties of catalyst depend on the synergism effect between Pt, TiO_2 and natural zeolite, intrinsic situation is comparatively complicate because of various components contained in the natural zeolite in this experimental system. The mechanism of pH effect on photocatalytic decolorization should be further investigated.

3.3.7. *The repeatability of photocatalyst activity*

The repeatability of the photocatalytic activity for the photocatalyst is a very important parameter to assess the photocatalyst practicability. The related experiments have been carried

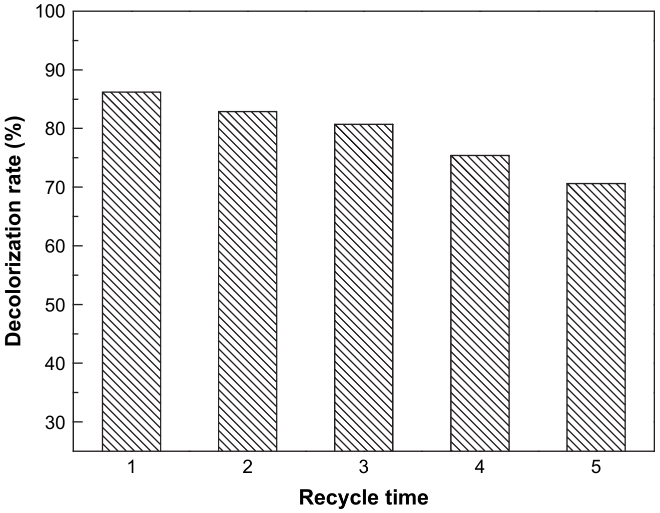

Fig. 9. Effect of recycle time on the decolorization rate of methyl orange solution. Catalyst: 1.5 wt.% Pt–TiO_2/zeolite; dosage: 2 g/l; MO concentration: 20 mg/l; pH 6.2; irradiation time: 30 min.

out on the silver supported TiO_2 doctor blade films for degradation of methyl orange by Arabatzis et al. [45] and the TiO_2 immobilized on pumice stone for the destruction of acid orange 7 by Subba Rao et al. [46]. In our experiment, the repeatability of the photocatalytic activity of 1.5 wt% Pt–TiO_2/zeolite was performed. The results are presented in Fig. 9. The concentration of methyl orange was kept constant (20 mg/l) with pH 6.2 and 30 min irradiation time, and the photocatalyst was recycled after filtrating and heating treatment at 200 °C for 2 h at every cycle. It can been seen that the decolorization rate decreases from 86.2% to 70.6% after five cycles, maintained 81.9% of initial decolorization rate, indicating that the photocatalytic activity has a better repeatability. The decrease of decolorization rate was explained by the TiO_2 and Pt loss from the support surfaces and the fouling of the catalyst by the by-products of degradation [46]. The TiO_2 and Pt attached on the natural zeolite maybe lost during filtrating and washing processes, on the other hand, it is difficult that the by-products of degradation adsorbed on the photocatalyst surfaces are cleaned thoroughly, which influences the surface properties of the photocatalyst. The heat treatment will cause the elimination of by-products of degradation, which is beneficial to refresh the photocatalyst surfaces resulting in the recovery of catalytic activity, but the heat treatment will also induce the catalyst aggregation after several recycles resulting in the decrease of surface area, finally leading to the decrease of photocatalytic efficiency.

4. Conclusion

Pt modified TiO_2 loaded on natural zeolites has been prepared by sol–gel technique and photoreductive deposition method. Pt doping is helpful to the enhancement of photocatalytic decolorization and the optimal Pt doping is about 1.5 wt.% with 86.2% of decolorization rate under 30 min of irradiation time. This enhancement is attributed to the Pt particles action as electron traps to inhibit the recombination of photogenerated electron and hole pair. The decolorization rate is influenced strongly by pH and the addition of H_2O_2. The catalyst shows higher activities at lower pH than at higher pH due to the strong adsorption of methyl orange on the catalyst surface. The catalyst has a good repeatability after five cycles.

Acknowledgements

This work was jointly supported by the National Natural Science Fund of China (No. 50082003, No. 50372022) and Provincial Natural Science Foundation of Fujian, China (No. D0010011).

References

[1] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chem Rev 1995;69:69–96.

[2] Linsebigler AL, Lu GQ, Yates Jr JT. Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chem Rev 1995;95: 735–58.

[3] Bahnemann D. Photocatalytic water treatment: solar energy applications. Sol Energy 2004;77:445–59.

[4] Herrmann JM. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catal Today 1999;53:115–29.

[5] Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. J Photochem Photobiol C Photochem Rev 2000;1:1–21.

[6] Litter MI. Heterogeneous photocatalysis: transition metal ions in photocatalytic systems. Appl Catal B Environ 1999;23:89–114.

[7] Hachem C, Bocquillon F, Zahraa O, Bouchy M. Decolourization of textile industry wastewater by the photocatalytic degradation process. Dyes Pigments 2001;49:117–25.

[8] Fernández A, Lassaletta G, Jiménez VM, Justo A, González-Elipe AR, Herrmann JM, et al. Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. Appl Catal B Environ 1995;7:49–63.

[9] Ao CH, Lee SC. Combination effect of activated carbon with TiO_2 for the photodegradation of binary pollutants at typical indoor air level. J Photochem Photobiol A Chem 2004;161:131–40.

[10] Robert D, Piscopo A, Heintz O, Weber JV. Photocatalytic detoxification with TiO_2 supported on glass-fibre by using artificial and natural light. Catal Today 1999;54:291–6.

[11] Ooka C, Yoshida H, Suzuki K, Hattori T. Highly hydrophobic TiO_2 pillared clay for photocatalytic degradation of organic compounds in water. Microporous Mesoporous Mater 2004;67:143–50.

[12] (a) Xu Y, Langford CH. Enhanced photoactivity of a titanium(IV) oxide supported on ZSM5 and zeolite A at low coverage. J Phys Chem 1995;99:11501–7;
(b) Xu Y, Langford CH. Photoactivity of titanium dioxide supported on MCM41, zeolite X, and zeolite Y. J Phys Chem B 1997;101:3115–21.

[13] Mohamed RM, Ismail AA, Othman I, Ibrahim IA. Preparation of TiO_2–ZSM-5 zeolite for photodegradation of EDTA. J Mol Catal A Chem 2005;238:151–7.

[14] Anpo M, Takeuchi M, Ikeue K, Dohshi S. Design and development of titanium oxide photocatalysts operating under visible and UV light irradiation. The applications of metal ion-implantation techniques tosemiconducting $TiO_2$and Ti/zeolite catalysts. Curr Opin Solid State Mater Sci 2002;6:381–8.

[15] Durgakumari V, Subrahmanyam M, Subba Rao KV, Ratnamala A, Noorjahan M, Tanaka K. An easy and efficient use of TiO_2 supported HZSM-5 and TiO_2 + HZSM-5 zeolite combinate in the photodegradation

of aqueous phenol and *p*-chlorophenol. Appl Catal A Gen 2002;234: 155–65.

[16] Zhu CM, Wang LY, Kong LR, Yang X, Wang LS, Zheng SJ, et al. Photocatalytic degradation of azo dyes by supported $TiO_2 + UV$ in aqueous solution. Chemosphere 2000;41:303–9.

[17] Shankar MV, Cheralathan KK, Arabindoo B, Palanichamy M, Murugesan V. Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by $TiO_2/H\beta$. J Mol Catal A Chem 2004;223:195–200.

[18] Reddy EP, Davydov L, Smirniotis P. TiO_2-loaded zeolites and mesoporous materials in the sonophotocatalytic decomposition of aqueous organic pollutants: the role of the support. Appl Catal B Environ 2003;42:1–11.

[19] Fukahori S, Ichiura H, Kitaoka T, Tanaka H. Capturing of bisphenol A photodecomposition intermediates by composite TiO_2–zeolite sheets. Appl Catal B Environ 2003;46:453–62.

[20] Chen H, Matsumoto A, Nisimiya N, Tsutsumi K. Preparation and characterization of TiO_2 incorporated Y-zeolite. Colloids Surf A Physicochem Eng Asp 1997;157:295–305.

[21] Anandan S, Yoon M. Photocatalytic activities of the nano-sized TiO2-supported Y-zeolites. J Photochem Photobiol C Photochem Rev 2003;4:5–18.

[22] Wang XX, Lian WH, Fu XZ, Basset JM, Lefebvre F. Structure, preparation and photocatalytic activity of titanium oxides on MCM-41 surface. J Catal 2006;238:13–20.

[23] Chuan X, Hirano M, Inagak M. Preparation and photocatalytic performance of anatase-mounted natural porous silica, pumice, by hydrolysis under hydrothermal conditions. Appl Catal B Environ 2004;51:255–60.

[24] Li F, Jiang Y, Yu L, Yang Z, Hou T, Sun S. Surface effect of natural zeolite (clinoptilolite) on the photocatalytic activity of TiO_2. Appl Surf Sci 2005;252:1410–6.

[25] Huang ML, Xu CF, Wang LL, Lin JM, Wu JH. Preparation and photocatalytic activities of TiO_2 loaded natural zeolites photocatalyst. Acta Mineral Sinica 2004;24:329–32.

[26] Li FB, Li XZ. The enhancement of photodegradation efficiency using Pt–TiO_2 catalyst. Chemosphere 2002;48:1103–11.

[27] Arabatzis IM, Stergiopoulos T, Andreeva D, Kitova S, Neophytides SG, Falaras P. Characterization and photocatalytic activity of Au/TiO_2 thin films for azo-dye degradation. J Catal 2003;220:127–35.

[28] Herrmann JM, Tahiri H, Ait-Ichou Y, Lassaletta G, González-Elipe AR, Fernández A. Characterization and photocatalytic activity in aqueous medium of TiO_2 and Ag-TiO_2 coatings on quartz. Appl Catal B Environ 1997;13:219–28.

[29] Chen LC, Tsai FR, Huang CM. Photocatalytic decolorization of methyl orange in aqueous medium of TiO_2 and Ag–TiO_2 immobilized on γ-Al_2O_3. J Photochem Photobiol A Chem 2005;170:7–14.

[30] Hufschmidt D, Bahnemann D, Testa JJ, Emilio CA, Litter MI. Enhancement of the photocatalytic activity of various TiO_2 materials by platinisation. J Photochem Photobiol A Chem 2002;148:223–31.

[31] Anpo M, Takeuchi M. The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation. J Catal 2003;216:505–16.

[32] Senthilkumaar S, Porkodi K, Gomathi R, Geetha Maheswari A, Manonmani N. Sol–gel derived silver doped nanocrystalline titania catalysed photodegradation of methylene blue from aqueous solution. Dyes Pigments 2006;69:22–30.

[33] Baiocchi C, Brussino MC, Pramauro E, Prevot AB, Palmisano L, Marci G. Characterization of methyl orange and its photocatalytic degradation products by HPLC/UV–VIS diode array and atmospheric pressure ionizationquadrupole ion trap mass spectrometry. Int J Mass Spectrom 2002;214:247–56.

[34] Guettai N, Ait Amar H. Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part II: kinetics study. Desalination 2005;185:439–48.

[35] Nam W, Kim J, Han G. Photocatalytic oxidation of methyl orange in a three-phase fluidized bed reactor. Chemosphere 2002;47:1019–24.

[36] Al-Qaradawi S, Salman SR. Photocatalytic degradation of methyl orange as a model compound. J Photochem Photobiol A Chem 2002;148: 161–8.

[37] Cao JJ. Study on Crystal Structure of Modified Mordenite. Spectrosc Spectal Anal (Chinese) 2004;24:251–4.

[38] Majdan M, Kowalska-Ternes M, Pikus S, Staszczuk P, Skrzypek H, Zieba E. Vibrational and scanning electron microscopy study of the mordenite modified by Mn, Co, Ni, Cu, Zn and Cd. J Mol Struct 2003;649:279–85.

[39] Korkuna O, Leboda R, Skubiszewska-Zieba J, Vrublevs'ka T, Gun'ko VM, Ryczkowski J. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. Microporous Mesoporous Mater 2005;87:243–54.

[40] Wang Y, Hong C. Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO_2 suspensions. Water Res 1999;33:2031–6.

[41] Konstantinou IK, Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. Appl Catal B Environ 2004;49:1–14.

[42] Irmak S, Kusvuran E, Erbatur O. Degradation of 4-chloro-2-methylphenol in aqueous solution by UV irradiation in the presence of titanium dioxide. Appl Catal B Environ 2004;54:85–91.

[43] Sakthivel S, Neppolian B, Shankar MV, Arabindoo B, Palanichamy M, Murugesan V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. Sol Energy Mater Sol Cells 2003;77:65–82.

[44] Muruganandham M, Swaminathan M. Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2–UV process. Dyes Pigments 2006;68:133–42.

[45] Arabatzis IM, Stergiopoulos T, Bernard MC, Labou D, Neophytide SG, Falaras P. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl Catal B Environ 2003;42:187–201.

[46] Subba Rao KV, Subrahmanyam M, Boule P. Immobilized TiO_2 photocatalyst during long-term use: decrease of its activity. Appl Catal B Environ 2004;49:239–49.