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# Synthesis of nanosize MCM-41 loaded with TiO<sub>2</sub> and study of its photocatalytic activity

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#### ABSTRACT

In recent years, nanosized mesoporous materials have received significant attention due to their impact in different processes. Several diverse applications of these materials, e.g. high density magnetic recording, magnetic fluids, magnetic refrigeration as well as in photocatalysis, solar cells, photosensors, have triggered considerable research activities in the area of nanotechnology. In this work, nanosize MCM-41 was synthesized and loaded then with TiO<sub>2</sub> using tetra butoxy titanium (TBT). As prepared TiO<sub>2</sub> loaded materials was investigated by using X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR). The photocatalytic activity of the prepared TiO<sub>2</sub> loaded MCM-41 was finally evaluated by the degradation of methyl orange under irradiation of UV light. The result showed that TiO<sub>2</sub> loaded on nanosize MCM-41 has higher photocatalytic activity than that of TiO<sub>2</sub>.

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#### 1. Introduction

The discovery of MCM-41 mesoporous molecular sieves has allowed an immense scope for many to work on this new type of materials, with uniform size and shape of the pores, arranged in different ways and with a very high surface area and adsorption capacity. Incorporation of heteroatoms into the framework or onto the wall of mesoporous silicate can increase the amounts of defects, the acidity or basicity, the redox property, and thus improve the catalytic ability of silicate. Many works concerning the incorporation of transition metals [1–3] and some main group elements such as B, Ga and Indium

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0749-6036/\$ – see front matter © 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.spmi.2008.12.024 etc. into the wall of MCM41 by direct synthesis, ion exchange or impregnation method have been reported [4–6].

Modification of the internal surfaces in these porous materials was also possible with metal oxide surface groups such as titanium dioxide, a large band-gap semiconductor and versatile photocatalyst. The photocatalytic degradation (PCD) of the organic pollutants by  $TiO_2$  photocatalysts, nanoscaled or modified, has attracted considerable attention in waste treatment due to its high PCD rate for various organic molecules [7–10]. But the difficulties in recycling and pre-concentration restrict utilization of the finer  $TiO_2$  particles. Thus, the  $TiO_2$  nanoparticles, have been supposed to be fixed on the inert supports for practical applications. Synthesis and application of heteroatoms-containing mesoporous silicate have attracted great interest in material science [10–17].

In this work, the nano-sized MCM-41 was synthesized and used as a support for TiO<sub>2</sub> loading. Considering that the most of the PCD reactions take place at the surface of the photocatalyst compound, it thus will be worthwhile to investigate the surface or interface effect between nanosized MCM-41 and TiO<sub>2</sub>. To reveal this interaction, the morphology changes and the bond vibrations have been investigated systematically before and after TiO<sub>2</sub> loading. In order to examine the photocatalytic activity of the as prepared sample, the kinetic process of the PCD reaction of methyl orange (MO) has been measured.

#### 2. Experimental

Tetraethyl orthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) were procured from Aldrich. Tetra methyl ammonium hydroxide (TMAOH) and  $Ti(OC_4H_9)_4$  (98%) were purchased from Fluka and methyl orange (MO) from merck.

In a typical synthesis of nanosize Si-MCM-41, TMAOH (14.08 g) in 10 mL distilled water was added under constant stirring to TEOS (20.8 g) and the mixture was allowed to stir for 1 h. Then a solution of CTAB (20 g in 98 mL water) was added. The composition of the resultant gel was SiO<sub>2</sub>: 0.33TMAOH: 0.55CTAB: 60H<sub>2</sub>O. The gel was transferred to a Teflon-lined autoclave and kept at 100 °C for 4 days. The solid Si-MCM-41 obtained was filtered, washed and dried at 100 °C in air and calcined at 550 °C.

A transparent TiO<sub>2</sub> solution was prepared by slowly instilling the Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> and ethanol mixture into diluted HCl aqueous solution. In a typical synthesis of TiO<sub>2</sub>/nano-MCM-41, 2 g of nanosize MCM-41 was added to 3 mL of the resultant TiO<sub>2</sub> solution. The content of TiO<sub>2</sub> in MCM-41in our prepared samples was estimated to be 5 wt%. After drying, the loaded catalyst was calcined at 500 °C. As a comparison, pure TiO<sub>2</sub> nanopowders were also prepared using the same procedure except for the addition of nanosized MCM-41.

The patterns and average crystal size of the samples were collected from an X-ray SEISERT Argon 3003 PTS diffractometer using nickel-filtered XD-3a Cu–K $\alpha$  radiation ( $\lambda = 1.5418$  A). The FT-IR spectra were recorded using a BOMEM MB100 spectrometer. The TEM measurements were performed on a Philips EM208 microscope operated at 100 kV. The sample was prepared by dispersing the powder in ethanol. Imaging was enabled by depositing few drops of suspension on to a carbon coated 400 mesh Cu grid. The solvent was allowed to evaporate before imaging. To compare the photoactivity of different catalysts, the kinetic processes of the PCD of MO, a typical azo dye in an aqueous system were studied using a UV-visible Hitachi spectrophotometer model U-2101 PC.

During the PCD experiments of MO, 15 mL of MO aqueous solution with a known initial concentration ( $C_0 = 30, 40 \text{ mg/L}$ , respectively) was mixed with 0.03 g of TiO<sub>2</sub>/nano-MCM-41, into a cell of 25 mL. The obtained suspension was then illuminated under 250 W high-Hg lamp with a 254–365 nm wavelength at room temperature. No proceeding molecular oxygen was added into the system in order to check the real photoactivity of the catalyst in the usual industrial conditions. The light intensity was kept to be the same for all experiments and the kinetic process of PCD of MO (color removal) was investigated using a UV-754 spectrophotometer at 463 nm light.

#### 3. Results and discussion

The small angle powder X-ray diffraction patterns of MCM-41 crystallized at 550 °C for 5 h and as prepared MCM-41 loaded by TiO<sub>2</sub> nanoparticles were displayed in Fig. 1(a), (b). The results indicate



Fig. 1. Comparison of the XRD patterns of (a) nano MCM-41 (b)TiO<sub>2</sub>-loaded nano MCM-41.

that the X-ray patterns are very similar with a very intense peak assigned to reflections at (100) and two additional peaks with low intensities at (110) and (200) reflections, respectively, and can be indexed to hexagonal lattice. Crystallinities of TiO<sub>2</sub> incorporated Si-MCM-41 were close to the parent material, though some loss in intensities of the peaks was observed upon loading TiO<sub>2</sub> with as evidenced by XRD. These results are quite in line with those reported in literature [18–20]. The crystallite size of TiO<sub>2</sub> loaded MCM-41 calculated through the XRD results indicated that small size of quantum dots (<5-9 nm) was achieved. Standard reference identification for anatase TiO<sub>2</sub> phase (JCPDS no. 21-1272) and those for rutile phase (JCPDS no 77-0441) were considered.

FT-IR spectra in Fig. 2 shows (a) as-synthesized nano-MCM-41 using TEOS and (b) TiO<sub>2</sub>/nano-MCM-41. The FTIR spectrum of MCM-41, as depicted in Fig. 2 shows two weak bands at 3365 and 3298 cm<sup>-1</sup> that are characteristic of the NH<sub>2</sub> (NH or OH vibrations) and two bands at 2922 and 2853 cm<sup>-1</sup> characteristic of asymmetric and symmetric vibrations of the CH<sub>2</sub> groups of the ethyl chain of silvlating agent before TiO<sub>2</sub> loading. This result demonstrate the fully silvlated Si-MCM-41 sample is of type III without any observation of pore filling or capillary condensation. Appearance of broad and intense vibrations bands at 3415, 3300 and 2950, 2853 cm<sup>-1</sup> in the FTIR spectrum of TiO<sub>2</sub>/nano-MCM-41 comparing with the raw MCM-41 demonstrate that the surface modified MCM-41 is very hydrophobic without significant adsorption of water in the whole vapor pressure range, but with a good capability of adsorbing organic compounds produced from Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> hydrolysis. This is of particular importance in designing selective adsorbents for environmental applications, such as the removal of volatile organic compounds (VOCs) in the presence of high humidity and adsorption of organics from wastewater. The broad absorption band at about 1332–1460 cm<sup>-1</sup> and band covered at the range of 957 to 905 cm<sup>-1</sup> in the FTIR spectrum of TiO<sub>2</sub>/nano-MCM-41 comparing with the raw MCM-41, can be ascribed to the stretching vibrations of Ti-O-Si, in similarity to the results reported by Liu et al. [20].

TEM images in Fig. 3(a), (b), (c) shows the typical image of as prepared– nano-MCM-41 and  $TiO_2/MCM$ -41. As shown in Fig. 3(a) for nano MCM-41, the size of MCM-41 nanoparticles and hexagonal structures of Si-MCM-41 can be observed. Fig. 3(b),(c) shows that  $TiO_2$  nanoparticles are aggregated outside MCM-41and their particle size were about 5–10 nm.

The photocatalytic activity of  $TiO_2/MCM-41$  system by studying the photoreduction of methyl orange is sown in Fig. 4. Accordingly, under UV irradiation of  $TiO_2/nanosized MCM-41$ , the conduction band electron can be removed quickly from the  $TiO_2$  site before charge recombination, because the



Fig. 2. IR spectra of as synthesized (a) nano MCM-41, (b) nano-MCM-41 loaded with TiO<sub>2</sub> particle.



Fig. 3. TEM images of as synthesized (a) nano MCM-41; (b), (c) nano-MCM-41 loaded with TiO<sub>2</sub> nanoparticles.

electron-rich MCM-41 surface functions as a hole scavenger [18–20]. This is the reason why the free  $TiO_2/MCM$ -41 catalyzes the photoreduction of methyl orange (Fig. 4). The curve of simple MO aqueous solution at the concentration  $C_0$  (not shown in this article) showed that the nano-MCM-41 support is photo-inert in the PCD process of MO. Therefore, the degradation curve of raw nano-MCM-



Fig. 4. Comparison of photoreduction rate of MO in the presence of TiO<sub>2</sub>/MCM-41 at different time.



**Fig. 5.** Evolution of the MO concentration vs. *t* for nano  $TiO_2/MCM-41$  at different  $C_0$ .

41 was subtracted from the apparent degradation curves of  $TiO_2/nano$  MCM-41, in order to achieve the adjusted reaction rate. That means that the degradation of MO on raw nano-MCM-41 was treated as the background of the PCD process on  $TiO_2/nano$  MCM-41. As the effect of pollutant concentration is of importance in any process of water treatment, it was necessary to investigate its dependence. The effects of  $C_0$  on the evolution of the PCD of MO by  $TiO_2/nano$  MCM-41 were shown in Fig. 5.

Generally, the PCD of the organic chemical always tends to follow pseudo-first order kinetics, which has been widely used in both aqueous and gas systems. Therefore, the rate of the pseudo-first-order reaction was calculated by a linear plot of  $\ln (C_0/C)$  versus *t* and the values of  $k_1$  at various degradation degree of MO (80,85,95%) are summarized in Table 1 as a function of initial concentration  $C_0$ .

Seen from Table 1, the TiO<sub>2</sub>/MCM-41 displays higher photocatalytic activity than pure TiO<sub>2</sub> nano powders especially at low concentration of MO, that may be caused by the super adsorption capability of the nano MCM-41 support. Comparing the value of  $k_1$  at different degradation degree of the initial concentration, we find that the TiO<sub>2</sub> –MCM-41 shows a higher efficiency in the later period of the PCD process. for example, when  $C_0 = 16 \text{ mg/L}$ , the TiO<sub>2</sub>/MCM-41 needs 45 min to achieve 80% degradation

C <sub>0</sub> (mg/L)	TiO <sub>2</sub> -MCM-41			Pure TiO <sub>2</sub>		
	80%	85%	95%	80%	85%	95%
4	1597/0	0350/0	0382/0	0432/0	1097/0	1196/0
8	1017/0	0387/0	0391/0	0407/0	0859/0	0961/0
12	0631/0	0432/0	0562/0	0532/0	0618/0	06259/0
16	0398/0	0381/0	0409/0	0481/0	0429/0	0411/0
20	0261/0	0281/0	0331/0	0381/0	0285/0	02685/0
$C_0 (mg/L)$	01810/0	0228/0	0288/0	0328/0	0163/0	0189/0

Table 1 The fitted pseudo-first-order rate constant  $(k_1)$  of different catalysts at various initial concentration of MO  $(C_0)$ .

of MO which is 5 min later than the pure TiO<sub>2</sub> nanopowders. when it comes to the 85% degradation, TiO<sub>2</sub>/MCM-41 only needs 50 min, which is 5 min ahead of the pure TiO<sub>2</sub> and when in view of 90% degradation, the  $TiO_2/MCM$ -41 shows 23 min quicker that the pure  $TiO_2$  nanopowders.

#### 4. Conclusion

In this work, photocatalytic activity of  $TiO_2$ /nano MCM-41 was studied. As a result, the growth of TiO<sub>2</sub> particles is restrained by the nano MCM-41 surface. Infrared analysis confirms that the TiO<sub>2</sub> colloid particles combine with the active sites of nano –MCM-41, by formation of Ti–O–Si bonds which make loading of the TiO<sub>2</sub>more durable than simple physical combination. Also, the FT-IR confirms that the samples, which were prepared by a silica source, gave an MCM-41 phase. TEM images show that the well ordered mesoporous arrangement was clearly visible with a pore size of 5–7 nm. The PCD results show that, the TiO<sub>2</sub>/nano-MCM-41 displays higher photocatalytic efficiency at low initial which is 6 min ahead of the pure TiO<sub>2</sub>in higher concentration and tends to benefit in avoiding the passivation of TiO<sub>2</sub> in the later period of the PCD process. TiO<sub>2</sub> loaded MCM-41 catalysts exhibited discernable photocatalytic activities in visible light, and their photocatalytic activities increased considerably with increasing TiO<sub>2</sub> loading up to 33 wt%. Further increase in TiO<sub>2</sub> loading enhanced photocatalytic activity slightly.

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