

Synthesis, characterization and photocatalytic properties of titania-modified mesoporous silicate MCM-41

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A series of titania modified mesoporous silicate MCM-41 (MCM-TiO₂) samples with variable Ti/Si ratios have been synthesized from tetrabutyltitanate and calcined MCM-41. The samples were characterized by powder X-ray diffraction (XRD), FTIR spectroscopy, thermal analysis (DTA-TG), nitrogen adsorption-desorption at 77 K, transmission electron microscopy (TEM), and solid state diffuse reflectance UV-VIS spectroscopy. It was found that tetrabutyltitanate cocondensation occurred with pendant OH groups of MCM-41 leading to Si-O-Ti bonds so modifying the inner pore surface of MCM-41 after hydrolysis and calcination. In the titania modified MCM-41 samples, although titania species were in tetrahedral rather than octahedral coordination which is predominant in crystalline titania, it still exhibited good photocatalytic activity for oxidizing phenol to carbon dioxide and water.

Introduction

Since the discovery of the M41S family of periodic mesoporous molecular sieves by Mobil in 1992,^{1,2} the synthesis, characterization and potential uses of the new mesoporous molecular sieves are well established.³ MCM-41, a member of this family, possesses a highly ordered pore structure comprised of hexagonally packed cylindrical channels, and is characterized by high surface areas and narrow pore size distributions.^{4,5} Metals, metal oxides, semiconductor clusters, various metal complexes and even large organic molecules can be introduced into the channels of MCM-41 owing to its large pores and huge surface area.⁶ In MCM-41, an estimated³ 8–27% of silicon atoms are linked with pendant OH groups ≡Si-OH. Jacobs and coworkers⁷ reported the grafting of 3-mercaptopropyl groups onto the inner wall of MCM-41 through the pendant OH group. Sutra and Brunel⁸ modified the inner surface of MCM-41 with 3-chloropropyl groups by using 3-chloropropyltriethoxysilane as the precursor.

Titanium dioxide is well known as a large-bandgap semiconductor with photocatalytic activity. It has a large number of applications such as in environmental purification, decomposition of organic contaminants, generation of hydrogen gas, etc.⁹ Recently, there has been substantial interest in introducing titanium into mesoporous silica.¹⁰ Titanium-containing mesoporous materials have higher active surface areas (>200 m² g⁻¹) than pure titania, which makes them more effective. Two main types of Ti(IV)-modified MCM-41 mesoporous materials have been highlighted.¹¹ One type arises from Ti(IV) being embedded in the framework of MCM-41 by addition of a suitable Ti(IV) precursor to the MCM-41 synthesis system.^{12–15} The other is obtained by grafting titanium onto the MCM-41 inner surface wall by using an organometallic precursor such as Cp₂TiCl₂.¹⁶ The advantages in using the latter method are not only greater accessibility of grafting onto the mesoporous silicate, but also the titanium coordination can be adjusted by varying experimental conditions.¹⁷

In this work, the inner pore walls of MCM-41 were modified with titania using tetrabutyltitanate as the titanium precursor in reaction with calcined MCM-41. The as-synthesized samples were characterized by XRD, FTIR, DTA-TG, nitrogen adsorption-desorption at 77 K, TEM and UV-VIS

spectroscopy. The decomposition of phenol was carried out as a model reaction to investigate the photoactivity of titania modified MCM-41.

Experimental

Synthesis of MCM-41

MCM-41 was synthesized by mixing cetyltrimethylammonium bromide (CTAB), sodium hydroxide (A.R.), fumed SiO₂ (>99%) and deionized water. The molar composition of the gel subjected to hydrothermal synthesis was: 1CTAB:4SiO₂:1.9NaOH:200H₂O. The mixture was stirred for 2 h at room temperature and then heated at 373 K for 5 days in a stainless steel autoclave under static conditions. When the mesoporous silica growth process was complete, the white precipitate was collected by filtration, washed several times with deionized water and then air-dried overnight. A careful calcination procedure was followed to remove the surfactant CTAB. Calcination was performed by heating from room temperature to 873 K at 2 K min⁻¹ in air and then holding at 873 K for 6 h.

Titania modified MCM-41

1.0 g calcined MCM-41 was placed in a 250 ml round-bottom flask and 50 ml dry hexane (A.R.) and 5.0 ml tetrabutyltitanate (TBOT, A.R.) were added. The mixture was stirred and refluxed at 343 K for 4–24 h under nitrogen. The solid was separated from the mixture using centrifugation at a rate of 5000 rpm. It was washed repeatedly with dry ethanol until free from TBOT. The solid was then hydrolyzed in a beaker with 150 ml deionized water. The mixture was allowed to stir for 2 h, and the product then washed with deionized water, filtered off and air-dried at room temperature. After calcination at 673 or 773 K for 2 h, the white powder product MCM-TiO₂ was obtained.

Photocatalytic experiments

A typical reaction mixture consists of 8 ml 0.5% aqueous phenol solution and an appropriate amount of catalyst (0.8 g calcined titania modified MCM-41, 0.16 g anatase or 0.52 g

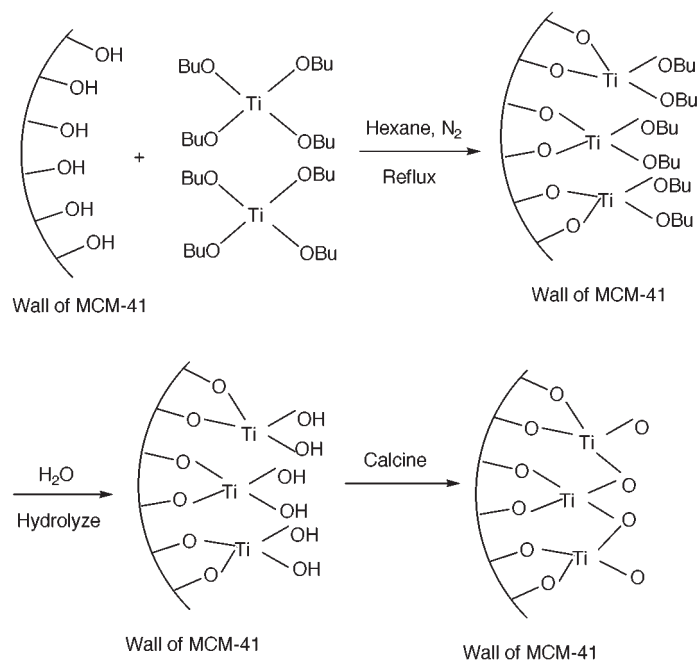


Fig. 1 Schematic of reactions between mesoporous silicate MCM-41 and tetrabutyltitanate.

titania–silica composite oxide (25 wt% TiO_2 –75 wt% SiO_2) in 400 ml deionized water. The system was stirred at room temperature, and irradiated with a 300 W high-pressure mercury vapor lamp in a water-cooled cylindrical jacket in the center of the reactor. After the photocatalytic reaction, 4 ml of the mixture was removed from the reactor and was diluted to 40 ml with deionized water in a tube. The transparent liquid was segregated from mixture by using high centrifugation (8000 rpm), and quantitatively analyzed by UV–VIS spectroscopy.

Characterization techniques

The Ti/Si molar ratio was measured using a Philips PW2400X X-ray fluorescence spectrometer. The X-ray diffraction patterns were collected on Rigaku D/max rB diffractometer, using $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation at 40 kV and 60 mA over the scan range 2θ 1.8–10°. FTIR spectra were recorded from KBr pellets (1 wt% sample and 99% KBr) using a Nicolet 7900 spectrophotometer. Thermogravimetric analyses were performed using a Netzsch STA-429 instrument under air with a heating rate of 10 K min^{-1} . N_2 adsorption–desorption isotherms at 77 K were conducted on a Micromeritics ASAP 2010 micropore analysis system. The samples were outgassed at 573 K for 4 h. Transmission electron microscopy images were obtained on a JEOL-2010CX microscope. UV–VIS spectra were measured on a PE Lambda 20 solid state UV–VIS spectrophotometer. Powder samples were loaded in a quartz cell and the spectra in the wavelength range 190–600 nm were collected.

Results and discussion

Fig. 1 summarizes the three steps of the reaction between mesoporous silicate MCM-41 and TBOT. The first step is the cocondensation of TBOT with pendant OH groups on the pore surface. No water is present at this stage in order to prevent TBOT hydrolysis. $=\text{Ti}-(\text{OBu})_2$ groups grafted on the wall of MCM-41 are then hydrolyzed to $=\text{Ti}-\text{OH}$ in the absence of TBOT in the pores of MCM-41 in the second step while in the final step, calcination of the powder, the hydroxy groups condense giving oxygen bridging bonds.

XRD

X-Ray powder diffraction patterns of the as-synthesized samples are shown in Fig. 2. The patterns show several Bragg peaks at low reflection angles between 1.8 and 10.0° , which are typical of MCM-41 materials. The strongest peak is indexed as the (100) reflection. The hexagonal unit cell length of MCM-41 is *ca.* 46.7 Å according to the formula³ $a = 2d_{(100)}3^{1/2}$. After calcination to remove surfactant CTAB, the intensity of the XRD pattern of MCM-41 increases significantly and shows better resolution due to some atomic rearrangement occurring within the mesoporous material during calcination.¹⁸ The XRD patterns of TiO_2 -modified MCM-41 samples [Fig. 2(c)–(d)] are free from crystalline TiO_2 and suggest retention of long-range order in the hexagonal phases. However the patterns suggest a slightly lower crystallinity than those of the unmodified MCM-41 since the other Bragg peaks (110), (200), (210) cannot be clearly observed by XRD.

FTIR

FTIR spectra of the calcined samples are shown in Fig. 3. In all samples, bands at 1080 and 795 cm^{-1} are clearly visible, which

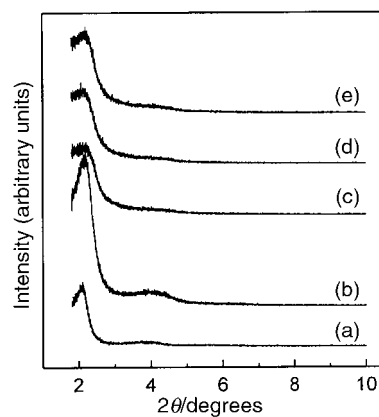


Fig. 2 XRD of (a) as-synthesized MCM-41, (b) calcined MCM-41, (c) TiO_2 -modified MCM-41, molar ratio Ti/Si = 0.1, (d) Ti/Si = 0.17 and (e) Ti/Si = 0.2.

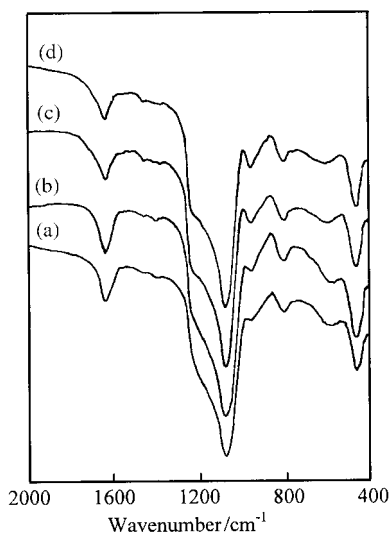


Fig. 3 FTIR spectra of (a) calcined MCM-41, (b) TiO₂-modified MCM-41, molar ratio Ti/Si=0.1; (c) Ti/Si=0.17 and (d) Ti/Si=0.2.

are assigned to the asymmetric and symmetric stretching vibrations, respectively, of framework Si–O–Si. The Si–O–Ti linkage stretching band appears at 950 cm⁻¹ for the modified MCM-41 samples, the intensity of which is enhanced with an increase of Ti/Si molar ratio. Additionally, the absence of crystalline titanium dioxide in the pore system of MCM-41 is further confirmed since there is no stretching band at 710 cm⁻¹ assignable to Ti–O–Ti.

DTA–TG

The results of thermal analysis are presented in Fig. 4. DTA and TG measurements were carried out in static air from room temperature to 1073 K. In TG the weight loss occurs in two steps. The first weight loss of ca. 16% below 423 K is attributed to the loss of water adsorbed in the pores while the second loss of 8% in the region 453–693 K corresponds to the condensation between hydroxy groups linked to titanium, with a corresponding strong exothermic peak appearing in the DTA curve. Beyond 873 K the framework of MCM-41 is progressively destroyed, registered as an endothermic process in the DTA curve.

N₂ adsorption–desorption isotherms

Nitrogen sorption isotherms at 77 K for the calcined samples are presented in Fig. 5. The isotherms can be classified as type IV according to the IUPAC convention, and are typical of mesoporous materials. A linear increase at low relative pressure indicates monolayer nitrogen adsorption in the mesoporous pores. When P/P_0 is between 0.2 and 0.3, a steep rise is due to capillary condensation inside the mesoporous pores.¹⁹ The subsequent long plateau at higher relative pressure, $0.4 <$

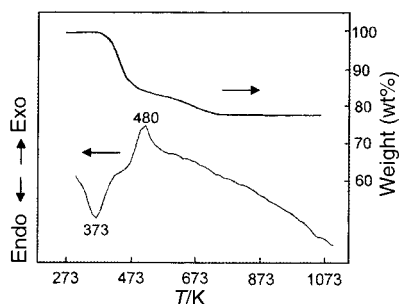


Fig. 4 DTA–TG of titania modified MCM-41 (as-synthesized Ti/Si=0.2).

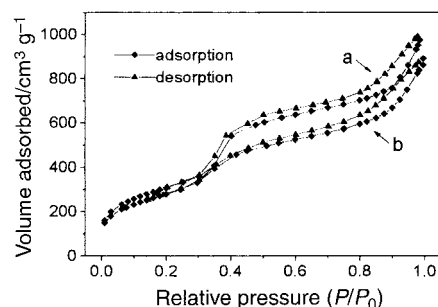


Fig. 5 Nitrogen adsorption–desorption isotherms at 77 K of (a) calcined MCM-41 and (b) calcined TiO₂-modified MCM-41, Ti/Si=0.2.

$P/P_0 < 0.8$, indicates the pore-filling is more restricted beyond the inflection point. There are no obvious differences in the shapes of the isotherms between MCM-41 and MCM-TiO₂. However, the specific surface area of MCM-TiO₂ is reduced by ca. 10% relative to MCM-41. A summary of results obtained from N₂ adsorption–desorption measurements is given in Table 1.

TEM

The transmission electron microscope lattice image and selected-area diffraction pattern of a titania modified mesoporous MCM-41 sample is shown in Fig. 6. TEM of the calcined sample shows that the (100) direction still retains a regular hexagonal array of uniform channels characteristic of mesoporous MCM-41. Each pore is surrounded by six neighbors and is of hexagonal structure, and unaffected by the presence of titania within. Furthermore, no crystalline titanium dioxide is observed.

Solid state UV–VIS spectra

Fig. 7 shows the solid state UV–VIS adsorption spectra of calcined titania modified MCM-41 and nanosized anatase. TiO₂ is a large bandgap semiconductor and the blue shift is attributed to the well known quantum size effect for semiconductors as the particle size decreases.²⁰ In this experiment, the band edge of 357 nm observed for titania modified MCM-41 is significantly blue shifted from the band edge of 385 nm for bulk anatase. Ti/Si ratios and calcination temperature have little effect on UV–VIS spectra, *i.e.* MCM-41 modified with different Ti/Si molar ratios and calcined either at 673 or 773 K, the UV–VIS spectra showing the same curve shape as well as band edge. It is notable that at wavelengths

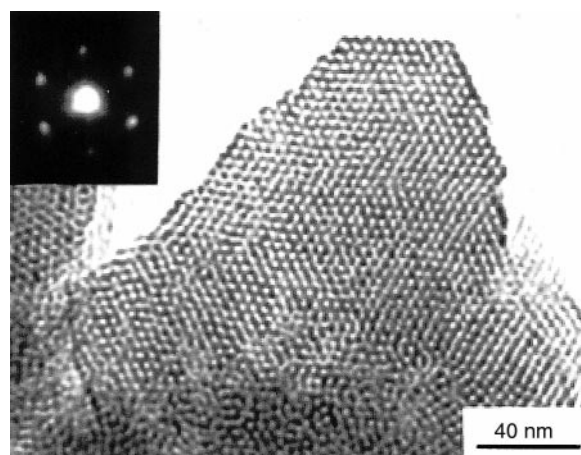


Fig. 6 TEM image and selected-area electron diffraction pattern of TiO₂-modified MCM-41, Ti/Si=0.2.

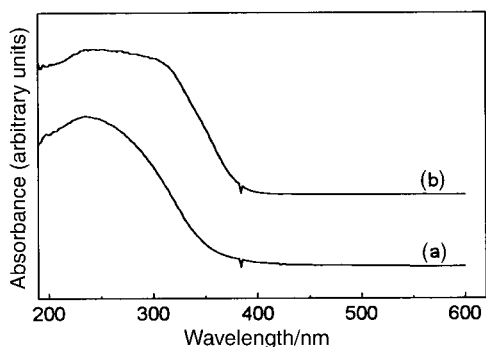
Table 1 N₂ adsorption–desorption data for calcined MCM-41 and MCM-TiO₂

Sample	Ti/Si molar ratio	BET surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	Main pore diameter (BJH)/nm
MCM-41	0	1127	1.61	4.4
MCM-TiO ₂	0.2	1020	1.45	4.3

Table 2 Activity of MCM-TiO₂ and other catalysts for phenol oxidation after 4 h reaction

Sample	Ti/Si ratio	Calcination temp./K	Decomposition (%)	Selectivity (%) ^a
MCM-41	0	873	— ^b	88.1
MCM-TiO ₂	0.1	673	31.4	84.6
MCM-TiO ₂	0.17	673	42.2	88.3
MCM-TiO ₂	0.2	673	42.6	89.7
		773	44.2	86.9
TiO ₂ (anatase, 27 nm)	∞	923	46.9	90.7
TiO ₂ -SiO ₂	0.33	873	60.3	87.4

^aDuring the process of photocatalytic reaction, phenol was oxidized to carbon dioxide and water with *p*-benzoquinone as a byproduct. ^bThe main photocatalytic products were 1,2- and 1,4-dihydroxybenzene and aldehydes; phenol does not undergo complete oxidation to carbon dioxide and water.

**Fig. 7** Solid state diffuse reflectance UV–VIS spectra of (a) TiO₂-modified MCM-41, Ti/Si=0.2 and (b) nanosized anatase (27 nm).

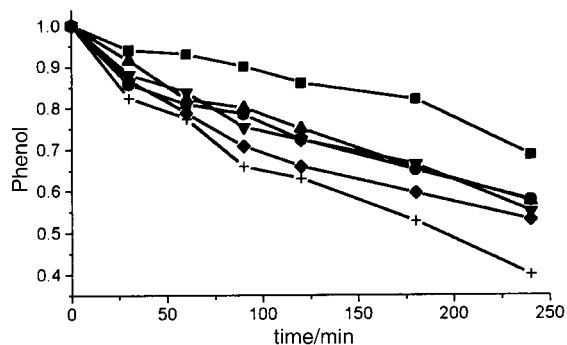
<300 nm, a wide adsorption peak appears in the spectrum of titania modified MCM-41 different to that of anatase.

Photodecomposition of phenol

TiO₂ used as a photocatalyst can decompose organic compounds. When TiO₂ (bandgap energy, $E_G=3.2$ eV) is illuminated with light with a wavelength <400 nm, excess electrons and positive holes are generated.^{21,22}



Aqueous phenol has been used as a test organic molecule to investigate the photoactivity of as-synthesized titania modified MCM-41. The oxidative decomposition of phenol is catalyzed

**Fig. 8** Decomposition of phenol by various catalysts: (■) Ti-modified MCM-41, Ti/Si=0.1; (●) Ti-modified MCM-41, Ti/Si=0.17; (▲) Ti-modified MCM-41, Ti/Si=0.2, calcined at 673 K; (▼) Ti-modified MCM-41, Ti/Si=0.2, calcined at 773 K; (◆) TiO₂ (anatase), 27 nm; (+) TiO₂-SiO₂ composite oxide.

by Ti^{IV}-OH[•] surface hydroxyl radicals.^{5,23} Photodecomposition results are shown in Table 2 and Fig. 8. Titanium dioxide in the modified MCM-41 is an amorphous monolayer on the inner surface of MCM-41 with Ti in tetrahedral coordination.²⁴ It shows a relatively high photocatalytic activity compared to crystalline TiO₂ such as anatase or a TiO₂-SiO₂ composite oxide, in which Ti is octahedral. Increasing the calcination temperature leads to a slight increase in the photocatalytic activity; the titanium dioxide species in the modified MCM-41 are in tetrahedral coordination and do not transform to anatase even at 773 K.

Conclusions

Modification of the pore walls of the mesoporous silicate MCM-41 has been achieved by treatment of calcined MCM-41 with the precursor tetrabutyltitanate. A combination of XRD, FTIR, thermogravimetry, nitrogen adsorption–desorption isotherm measurements at 77 K, TEM as well as solid state UV–VIS spectroscopy has been used to characterize the titania modified MCM-41 materials. The results show that an amorphous monolayer of TiO₂ modified the inner walls of MCM-41 and the maximum amount of Ti grafted onto MCM-41 corresponds to a molar ratio Ti/Si=0.2. Although the Ti in titania modified MCM-41 is tetrahedrally coordinated, it exhibits relatively high photocatalytic activity in oxidative decomposition of phenol.

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