Preparation, characterization and photocatalytic properties of singly and doubly titania-modified mesoporous silicate MCM-41 by varying titanium precursors

Shan Zheng,[a] Lian Gao,*[a] Qinghong Zhang,[a] Weiping Zhang[b] and Jingkun Guo[a]

[a]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China. E-mail: liangaoc@online.sh.cn
[b]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

A series of titania-modified MCM-41 have been synthesized from varying three kinds of titanium precursors [$Ti(OBu^n)_4$, $Ti(OBu^n)_3(acac)$, $Ti(OBu^n)_2(acac)_2$] respectively and mesoporous molecular sieve MCM-41, in which titania existed as single or double layers. The samples were characterized by powder X-ray diffraction (XRD), nitrogen adsorption–desorption at 77 K, ^{29}Si MAS NMR, FTIR and Raman spectroscopy, as well as by solid state diffuse reflectance UV–VIS spectroscopy. The titanium precursor was cocondensed with the active silanol groups of MCM-41 via Si–O–Ti bonds and the resulting titania modified the mesopore walls of MCM-41 after hydrolysis and calcination. In the titania-modified MCM-41 samples, although the titania species were in an amorphous state and in tetrahedral coordination rather than octahedral coordination, which exists extensively in crystalline titania, they exhibited high photocatalytic activity for the photodecomposition of phenol and the photoreduction of Cr(VI) to Cr(III).

Introduction

Self-assembled mesoporous silicate materials are formed by the condensation of silica and surfactant and have been the subject of great interest because of their potential uses as catalysts, hosts for inclusion compounds and molecular sieves.[1–5] MCM-41, one of the members of this family of materials, contains a regular hexagonal array of mesopores with a pore diameter of 2.0–10.0 nm depending on the synthesis conditions.[6,7] NMR studies reveal that MCM-41 contains many silanol groups (estimated 8–27%) after the template molecules have been removed.[2,8,9] These active silanols could not only act as functional groups in chemical reactions, but could also be utilized to anchor molecules having other functional groups. Thus the inner pore surface could be modified by grafting 3-mercaptopropyl or 3-chloropropyl moieties, prepared by using 3-mercaptopropyltriethoxysilane or 3-chloropropyltriethoxysilane as the precursors, respectively.[10,11] Furthermore, many kinds of transition metal oxides could also be used to modify the inner pore walls of MCM-41 such as titanium dioxide, manganese oxide and vanadium oxide by using organometallic precursors.[12–14]

Titanium dioxide is well known as a large bandgap ($\Delta E_g \geqslant 3.2$ eV) semiconductor with photocatalytic activity.[15] It has important applications in environmental purification, decomposition of organic contaminants, water splitting, etc.[16] More recently, introducing titanium species into mesoporous silicate materials has attracted much interest because the titanium-containing mesoporous materials have much higher active surface areas (>200 m^2 g^{-1}) in comparison to pure titania.[17] Adding appropriate and suitable Ti(IV) precursors in the MCM-41 synthesis system, Ti(IV) species may be embedded in the framework of MCM-41.[18–22] Another method of grafting titanium onto mesoporous materials is to modify the inner mesopores with a titanium precursor.[12,23,24] The advantage in using the latter method is the greater accessibility of the grafted species on the mesoporous silicate.[25]

In this work, $Ti(OBu^n)_4$, $Ti(OBu^n)_3(acac)$ and $Ti(OBu^n)_2(acac)_2$ were used as titanium precursors to prepare the singly and doubly titania-modified MCM-41. The titania-modified MCM-41 synthesized from three varying precursors were characterized by XRD, N$_2$ adsorption–desorption at 77 K, ^{29}Si MAS NMR, IR and Raman spectroscopy, and solid state UV–VIS spectroscopy. The photoactivity of the titania-modified MCM-41 is evaluated by using the photodecomposition of phenol and photoreduction Cr(VI) to Cr(III) as the test reactions.

Experimental

Synthesis of MCM-41

The synthesis of MCM-41 (Si/Al = 35) was carried out by using the hydrothermal method.[26] A mixture of cetyltrimethylammonium bromide, NaOH, NaAlO$_2$, fumed SiO$_2$ (99%) and distilled water in the molar ratio 1.0 : 1.9 : 0.1 : 4.0 : 200, CTAB : NaOH : NaAlO$_2$: SiO$_2$: H$_2$O was stirred for 2 h, then placed in a Teflon-lined stainless steel autoclave, and was heated at 373 K for 5 days under autogenous pressures. The product was filtered and washed with distilled water and then dried at ambient conditions. The as-synthesized MCM-41 was calcined in air at 873 K for 6 h to remove the surfactant CTAB.

Preparation acacH-modified $Ti(OBu^n)_4$

The acetylacetonate (acacH)-modified $Ti(OBu^n)_4$ compounds were synthesized previously according to literature techniques.[27] 10.0 g $Ti(OBu^n)_4$ was dissolved in 50 mL ethanol and 1.77 g (molar acacH/Ti = 0.6) or 5.88 g (molar acacH/Ti = 2)

acetylacetonate were added, respectively. The stirring was continued until the mixture formed a uniform yellow solution.

Synthesis of titania-modified MCM-41

2.0 g calcined MCM-41 was placed in a 250 mL round-bottom flask. 50 mL Ti(OBu^n)$_4$ (TBOT, 10.0 g)/ethanol, Ti(OBu^n)$_3$(acac)/ethanol or Ti(OBu^n)$_2$(acac)$_2$/ethanol solution were also added into it. The mixture was stirred and refluxed at 343 K for 24 h under a nitrogen atmosphere. The solid was separated from the mixture using centrifugation at a rate of 5000 rpm. It was washed repeatedly with dry ethanol until there was no superfluous titanium precursor. Then the solids were hydrolyzed in a beaker with 100 mL deionized water. After the product was washed by filtration and air-dried at 373 K, a careful calcination was achieved by heating from room temperature to 773 K at 1 K min^{-1} in air and then holding the temperature at 773 K for 2 h to condense hydroxyl groups and remove organic ligands. The as-synthesized samples were the singly titania-modifed MCM-41, which were recorded as s-MCM–TiO$_2$, s-MCM–TiO$_2$(a), or s-MCM–TiO$_2$(2a). If the singly modified MCM–Ti(OH)$_2$, which was synthesized from TBOT and MCM-41 after hydrolysis and before calcination, was cocondensed with the three different titanium precursors respectively instead of MCM-41 under the same experimental conditions, then the products were the doubly titania-modified MCM-41, and recorded as d-MCM–TiO$_2$, d-MCM–TiO$_2$(a), or d-MCM–TiO$_2$(2a). The samples synthesized from Ti(OBu^n)$_3$(acac) were designated as MCM–TiO$_2$(a), while the ones from Ti(OBu^n)$_2$(acac)$_2$ were designated as MCM–TiO$_2$(2a).

Photocatalytic experiments

A typical reaction mixture consisted of 400 mL of 100 ppm aqueous phenol solution and an appropriate amount of catalyst (2.0 g L^{-1} titania-modified MCM-41, 2.0 g L^{-1} TiO$_2$–SiO$_2$ mixed compound or 0.5 g L^{-1} anatase). The system was stirred at room temperature with O$_2$ bubbling (60 mL min^{-1}), a 300 W high-pressure mercury vapor lamp was used as the light source and placed into a water-cooled cylindrical jacket in the center of the reactor. A 4 mL extract of the mixture was removed from the reactor and was diluted to 40 mL with deionized water in a tube after 4 h. The transparent liquid was segregated from the mixture by using high centrifugation at a rate of 8000 rpm, and analyzed quantitatively by UV–VIS spectroscopy.

The experimental conditions for the photoreduction of Cr(VI) were similar to those for the photodecomposition of phenol. A 100 ppm Na$_2$Cr$_2$O$_7$ solution was used as the source of Cr(VI). Experiments were conducted with 2.0 g L^{-1} catalysts (except 0.5 g L^{-1}, for anatase) and in the presence of N$_2$ flow (100 mL min^{-1}) to remove dissloved O$_2$ in the solution. After 4 hours of reaction, a 4 mL extract of the suspension was withdrawn and diluted to 20 mL. After high certifugation, the upper transparent solution was analyzed for the remaining Cr(VI) at a wavelength of 370 nm using UV–VIS spectroscopy. The photocatalytic activity was evaluated by the decrease of Cr(VI) concentration after irradiation.

Characteristion techniques

The molar Ti/Si ratio was measured by using a Philips PW2400X X-ray fluorescence spectrometer. X-Ray diffraction patterns were collected on a Rigaku D/max rb diffractometer, using Cu-Kα ($\lambda = 0.15418$ nm) radiation at 40 kV and 60 mA over the scan range 1.8–10°. N$_2$ adsorption–desorption isotherms were measured at 77 K and BET surface areas of the calcined samples were performed on a Micromeritics ASAP 2010 micropore analysis system. The samples were outgassed at 573 K for 4 h. All ^{29}Si NMR spectra of samples were collected

at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO$_2$ rotors. ^{29}Si MAS NMR spectra were recorded at 79.5 MHz using a 0.8 μs π/8 pulse with a 4 s recycle delay and 2000 scans. FTIR spectra were recorded from KBr pellets using a Nicolet 7199 spectrophotometer. Raman spectra were obtained on a Dilor LabRam 00 Raman spectrophotometer. The UV–VIS spectra were measured on a PE Lambda 20 solid state UV–VIS spectrophotometer. Powder samples were loaded into a quartz cell and spectra were collected in the 190–600 nm wavelength range.

Results and discussion

The synthesis reaction for singly titania-modified MCM-41 from mesoporous silicate MCM-41 and the titanium precursors occurs in three steps. The first step is the cocondensation of the titanium precursors with silanols on the inner pore surface of MCM-41. No water is present at this stage in order to prevent TBOT or other titanium precursors hydrolyzing and introducing bulk TiO$_2$. Subsequently, the titanium precursors –R$_2$Ti–OBu (R = OBu or acac), which are grafted onto the walls of MCM-41, hydrolyze with water to –R$_2$Ti–OH when there is no excess titanium precursor in the mesopores. In the final step, the hydroxyl groups linked with Ti condense to titania and the titania modifies and anchors to the mesopore walls of MCM-41 after the calcination. With the utilization of –R$_2$Ti–OH, titanium precursors could modify the inner surface of MCM-41 once again. Finally, the titania could be described as a thin layer that is well dispersed on the walls of mesoporous MCM-41.

XRD

X-Ray powder diffraction patterns of MCM-41 and titania-modified MCM-41 are illustrated in Fig. 1. The strongest peak, which appeared between 1.8 and 10.0°, is indexed as the (100) reflection. The XRD patterns of titania-modified MCM-41 samples are free from crystalline TiO$_2$ and suggest that the hexagonal pore order was maintained after calcination in both singly and doubly titania-modified samples. It is believed that the presence of titania inside the pore walls introduced defects that could lead to collapse of the framework,[23] which decreased the peak intensity of (100) in titania-modified samples in comparison to unmodified MCM-41. The d-spacing of the titania-modified samples reduced from 42.0 to 39.8–40.6 Å (unmodified MCM-41) as a result of the introduction of titania.
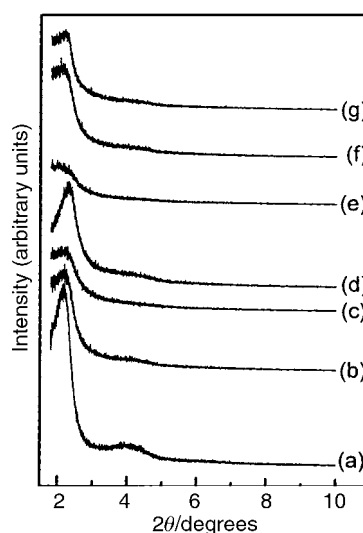

Fig. 1 XRD patterns of (a) MCM-41, (b) s-MCM–TiO$_2$, (c) s-MCM–TiO$_2$(a), (d) s-MCM–TiO$_2$(2a), (e) d-MCM–TiO$_2$, (f) d-MCM–TiO$_2$(a), (g) d-MCM–TiO$_2$(2a).
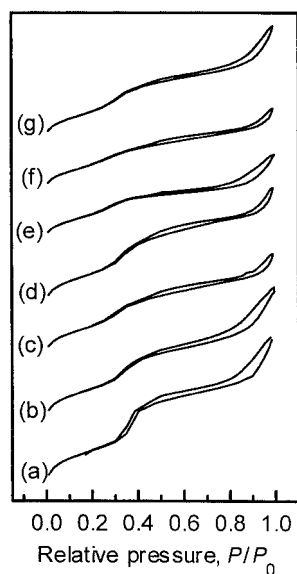
Fig. 2 Nitrogen adsorption–desorption isotherms at 77 K of (a) MCM-41, (b) s-MCM–TiO$_2$, (c) s-MCM–TiO$_2$(a), (d) s-MCM–TiO$_2$(2a), (e) d-MCM–TiO$_2$, (f) d-MCM–TiO$_2$(a), (g) d-MCM–TiO$_2$(2a).

Nitrogen adsorption–desorption

Fig. 2 shows the N$_2$ adsorption–desorption isotherms of template-free MCM-41 and titania-modified MCM-41. Little difference is observed between the N$_2$ sorption curves of mesoporous MCM-41 and those of MCM-41 containing titania, which suggests that the introduced titania didn't affect the mesopore structure of MCM-41. All materials give typical irreversible type IV sorption isotherms with an H1 hysteresis loop as defined by IUPAC.[28] The first adsorption step is accounted for by a monolayer adsorption of N$_2$ on the pore walls, which is followed by a sudden increase occurring at $P/P_0 > 0.3$. The increase suggests a large pore volume, and the sharpness of these steps reveals the uniformity of the mesopore size distribution. As in the case of grafted titania, the titania-modified MCM-41 materials reduced the sharpness, correspondingly the calculated BET surface areas and specific pore volume also decreased. The results are shown in Table 1.

For porous materials, the BJH pore size distribution, which is based on the Kelvin equation, is a useful method for the characterization of pore structure. Both MCM-41 and titania-modified MCM-41 samples show narrow pore size distributions. The main pore diameter of the mesopore did not indicate a remarkable decrease with the titania loading. The results suggest that the titania loading appears as a thin layer on the inner surface of the mesopore, not only for the single layer titania-modified MCM-41 but also for the double layer titania-modified MCM-41.

^{29}Si MAS NMR spectroscopy

Fig. 3 shows the ^{29}Si MAS NMR spectra of MCM-41 and titania-modified MCM-41. The ^{29}Si NMR of MCM-41 shows a
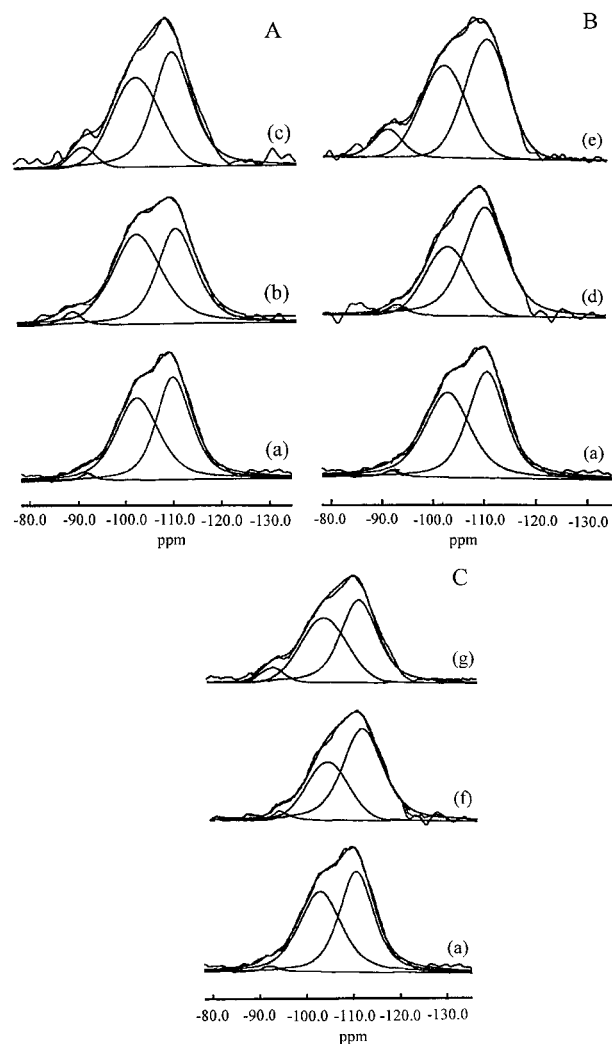

Fig. 3 ^{29}Si NMR spectra deconvoluted with Gaussian–Lorentzian lines. A: (a) MCM-41, (b) s-MCM–TiO$_2$, (c) d-MCM–TiO$_2$, B: (a) MCM-41, (d) s-MCM–TiO$_2$(a), (e) d-MCM–TiO$_2$(2a), C: (a) MCM-41, (f) s-MCM–TiO$_2$(a), (g) d-MCM–TiO$_2$(2a).

high-intensity signal at a chemical shift of -110 ppm, a shoulder at -102 ppm, and a very low intensity shoulder at -92 ppm, which is commonly assigned to Q^4 [Si(SiO)$_4$], Q^3 [Si(SiO)$_3$(OH)] and Q^2 [Si(SiO)$_2$(OH)$_2$] structural units, respectively.[6,29] The –OTi and –OH groups have a similar influence on the chemical shift of the central silicon atoms.[30] Thus, in the samples of titania-modified MCM-41, the resonance at -92 ppm, which is due to a silicon environment with a titanium next-nearest neighbor, has increased compared to the spectrum of MCM-41. After the curve is deconvoluted by Gaussian and Lorentzian line shapes, three peaks are clearly seen. The peak at -92 ppm increased markedly in s-MCM–TiO$_2$ and d-MCM–TiO$_2$ compared to MCM-41, as clearly demonstrated in Fig. 3A for the spectrum of d-MCM–TiO$_2$.

Table 1 The results of XRD and N$_2$ sorption for MCM-41 and titania-modified MCM-41

| | Samples | Ti/Si | XRD d_{100}/Å | A_{BET}/m^2 g^{-1} | V_{BJH}/cm^3 g^{-1} | D_{BJH}/Å |
				N$_2$ Sorption		
1	MCM-41	0	42.0	1128	1.61	27.6
2	s-MCM–TiO$_2$	0.20	40.4	1020	1.45	27.3
3	s-MCM–TiO$_2$(a)	0.17	40.1	939	1.14	27.4
4	s-MCM–TiO$_2$(2a)	0.15	39.8	993	1.29	26.5
5	d-MCM–TiO$_2$	0.32	39.8	836	1.00	26.8
6	d-MCM–TiO$_2$(a)	0.34	40.6	843	0.96	25.6
7	d-MCM–TiO$_2$(2a)	0.28	40.3	921	1.06	26.9

We think that the increased intensity of the peak at -92 ppm in d-MCM–TiO$_2$ cannot be attributed to the Ti–O–Si band increase, because in the synthesis of doubly titania-modified MCM-41, TBOT didn't react directly with the silanol groups in MCM-41. On the other hand, these facts reveal that the interaction between silicon and titanium becomes stronger with increasing Ti loading.

IR and Raman spectroscopy

The low-wavenumber region of the IR absorption spectrum has been used to characterize Ti-substituted molecular sieves.[4] Both MCM-41 and titania-modified samples exhibit the symmetric stretching vibration band at 801 cm^{-1} and the asymmetric vibration band at 1080 cm^{-1} of the tetrahedral SiO$_4^{4-}$ structural units. After titania-modification of the inner surface walls of MCM-41, an increase in the relative peak intensity at about 950 cm^{-1} is observed for all titania-modified samples, which is often used as evidence for the vibration of Ti–O–Si. After formation of the double layer titania-modified MCM-41, the intensity of Ti–O–Si did not increase accordingly. The intensity is similar to the single layer titania-modified MCM-41. It suggests that in singly titania-modified MCM-41 titania the precursors reacted with silanols, while in doubly titania-modified MCM-41 the titania precursors reacted with hydroxyl groups linked to Ti in singly titania-modified MCM-41. Table 2 shows the ratios of band vibrations of Ti–O–Si and Si–O–Si in titania-modified samples. It is inaccurate to simply compare the intensity of Ti–O–Si and Si–O–Si because the titania contents differ between the samples. However the ratio of Ti–O–Si/TiO$_2$ to Si–O–Si/SiO$_2$ can explain the titania situation on the inner surface of MCM-41. The decrease to 0.170–0.216 in doubly titania-modified MCM-41 compared to those in singly titania-modified samples illustrates that the titania is loaded onto the walls of the mesopore in two layers, that is in the second condensation procedure no new Ti–O–Si bonds are formed. Thus, the ratio decreases with increasing titania content.

Unfortunately, in the Raman spectra of titania-modified samples, very low intensity broadened signals assigned to SiO$_2$ can be observed.[31] Very intense Raman bands at 397, 515, 639 nm couldn't be detected for samples modified with titania, even for the double layer-modified samples, which are characteristic of TiO$_2$ anatase.[32] Thus, the titania on the mesoporous silicate walls is probably amorphous and not as easily recorded by Raman.

UV–VIS spectroscopy

UV–VIS spectroscopy has been extensively used to characterize the nature and coordination of Ti^{4+} ions in titanium. Fig. 4 shows the UV–VIS spectra of titanium-modified MCM-41 and anatase. A broad band between 200 and 300 nm centered at 230 nm could be observed in all samples. The band has been assigned to a charge-transfer transition between the oxygen ligands and a central Ti^{4+} ion with tetrahedral coordination (T_d).[33–35] All as-synthesized titania in titania-modified MCM-41 are in tetrahedral coordination, although they were
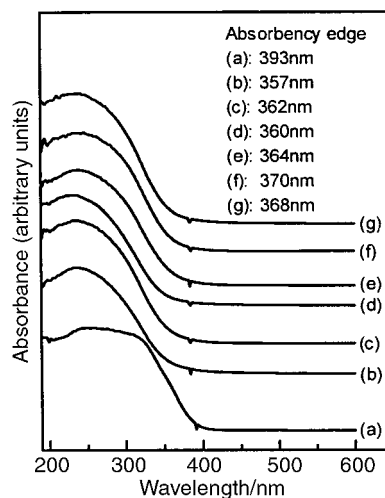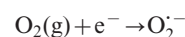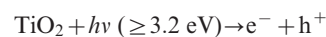
Fig. 4 Solid state diffuse reflectance UV–VIS spectra of (a) bulk TiO$_2$, (b) s-MCM–TiO$_2$, (c) s-MCM–TiO$_2$(a), (d) s-MCM–TiO$_2$(2a), (e) d-MCM–TiO$_2$, (f) d-MCM–TiO$_2$(a), (g) d-MCM–TiO$_2$(2a).

synthesized from titanium precursors with different Ti–O coordinaton.

The UV adsorption threshold is a strong function of titania cluster size for diameters less than 10 nm, which can be attributed to the well known quantum size effect for semiconductors.[36,37] A band edge of 357–362 nm could be observed in a singly titania-modified MCM-41, a significant blue shift from the band edge of 393 nm for calcined bulk anatase. For the doubly titania-modified MCM-41, the UV–VIS absorbency edge shifted to longer wavelength by 7–8 nm. The blue shift of the UV–VIS absorbance edge in titania-modified samples is due to the increased band energy of the titania, while the reason for the increase in band energy is the small size of the titania loading.

Photocatalytic study

1. Photodecomposition of phenol. Under irradiation with a wavelength less than 400 nm, titania could generate excess electrons and positive holes. O$_2$ traps the electrons and becomes O$_2^{\cdot-}$ with a high oxidizing power, and the positive holes, together with OH$^-$ in the solution, generate reactive OH$^{\cdot}$.[38,39]

$$TiO_2 + h\nu \ (\geq 3.2 \text{ eV}) \rightarrow e^- + h^+$$

$$e^- + h^+ \rightarrow \text{recombination}$$

$$O_2(g) + e^- \rightarrow O_2^{\cdot-}$$

$$h^+ + OH^- \rightarrow OH^{\cdot}$$

O$_2^{\cdot-}$ oxidized phenol to p-benzoquinone initially which was then mineralized to carbon dioxide and water. OH$^{\cdot}$ radicals attacked the benzene ring of phenol, and phenol was mineralized after ring opening.[40]
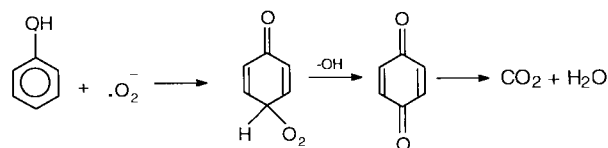
Table 3 illustrates the photoactivity of titania-modified MCM-41 for decomposition of phenol after a 4 h reaction. In general, samples of doubly titania-modified MCM-41 have

Table 2 Comparison of band vibrations (from FTIR) of Ti–O–Si at about 950 cm^{-1} and Si–O–Si at 1080 cm^{-1}

Samples	Ti–O–Si/Si–O–Si	(Ti–O–Si/TiO$_2$)/(Si–O–Si/SiO$_2$)^a
MCM-41	—	—
s-MCM–TiO$_2$	0.103	0.412
s-MCM–TiO$_2$(a)	0.092	0.449
s-MCM–TiO$_2$(2a)	0.097	0.549
d-MCM–TiO$_2$	0.080	0.170
d-MCM–TiO$_2$(a)	0.098	0.190
d-MCM–TiO$_2$(2a)	0.084	0.216

^{a}Ti–O–Si/TiO$_2$ means in titania-modified samples, Ti–O–Si in 1 mol TiO$_2$, Si–O–Si/SiO$_2$ is Si–O–Si in 1 mol SiO$_2$.
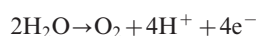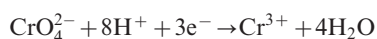
Table 3 Photoactivity of titania-modified MCM-41 for phenol decomposition after a 4 h reaction

Samples	Conversion (%)	Selectivity[a] (%)
No catalyst	18.0	—[b]
s-MCM–TiO$_2$	73.7	94.3
s-MCM–TiO$_2$(a)	71.9	95.3
s-MCM–TiO$_2$(2a)	81.9	96.3
d-MCM–TiO$_2$	83.0	99.0
d-MCM–TiO$_2$(a)	74.3	97.1
d-MCM–TiO$_2$(2a)	74.1	96.2
TiO$_2$–SiO$_2$(25 wt%TiO$_2$)[c]	70.6	96.0
Anatase[d]	100	98.0

[a]During the process of photocatalytic reaction, phenol was oxidized to carbon dioxide and water with by-product p-benzoquinone. [b]There are many intermediate products such as 1,2-dihydroxybenzene, 1,4-dihydroxybenzene and aldehydes; phenol does not undergo complete oxidation to carbon dioxide and water. [c]The Ti–Si compound was calcined at 873 K for 2 h, the BET surface area is 302.4 m^2 g^{-1}. [d]About 30 nm, the BET surface area is 8.5 m^2 g^{-1}.

Table 4 Photoactivity of titania-modified MCM-41 for Cr(VI) decomposition after a 4 h reaction

Samples	Conversion (%)
No catalyst	<2
s-MCM–TiO$_2$	40.9
s-MCM–TiO$_2$(a)	44.6
s-MCM–TiO$_2$(2a)	44.4
d-MCM–TiO$_2$	41.5
d-MCM–TiO$_2$(a)	47.6
d-MCM–TiO$_2$(2a)	49.8
TiO$_2$–SiO$_2$(25wt%TiO$_2$)[a]	8.6
Anatase[b]	57.8

[a]The Ti–Si complex compound was calcined at 873 K for 2 h, BET surface area is 302.4 m^2 g^{-1}. [b]30 nm, BET surface areas is 8.5 m^2 g^{-1}.

higher photoactivity than singly titania-modified MCM-41. The main reason why the decomposition of phenol doesn't rise remarkably, in parallel to the Ti/Si molar ratio increase between singly and doubly titania-modified MCM-41, is that titania exists as monolayers or bilayers on the internal surface. Furthermore the conversion of phenol is affected by titania-modified MCM-41 synthesized from different titanium precursors. Although the titania in modified MCM-41 is amorphous and in tetrahedral coordination, the compounds still exhibit relatively high photoactivity in comparison to crystalline nanosized anatase.

2. Photoreduction of Cr(VI) to Cr(III). Chromium is a frequent contaminant in waste water arising from industrial processes. Chromium occurs in two common oxidation states in nature, Cr(VI) and Cr(III). Hexavalent chromium is toxic to most organisms and is very soluble in water. On the other hand, Cr(III) is less toxic [less than 1% compared to Cr(VI)] and is readily precipitated in neutral or alkaline solutions.[41] Cr(VI) could be reduced to less harmful Cr(III) with photocatalytic titania-modified MCM-41 under UV irradiation. In the solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in the pH range 3–11, and the following equations show the reactions between CrO_4^{2-} and H_2O.[42,43]

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

So, the net reaction is:

$$4CrO_4^{2-} + 20H^+ \rightarrow 4Cr^{3+} + 10H_2O + 3O_2$$

Table 4 shows the results of Cr(VI) photoreduction to Cr(III) after 4 h irradiation. In conclusion, either single or doubly titania-modified MCM-41 exhibit similar activity for the photoreduction of Cr(VI). On the other hand, the photoactivity of doubly modified MCM-41 is a little higher than singly modified MCM-41, even though the BET surface areas decrease. Titania-modified MCM-41 samples resulted in a great increase in percentage conversion compared to the TiO$_2$–SiO$_2$ mixed compound, which possesses a high BET surface area of 304 m^2 g^{-1}.

In summary, the photoactivity test results on the photodecomposition of phenol and the photoreduction Cr(VI) to Cr(III) suggest that titania-modified MCM-41 synthesized from varying titanium precursors are relatively efficient photocatalysts, although the activity is lower than for nanosized crystalline anatase.

Conclusions

Singly and doubly titania-modified MCM-41 were prepared from mesoporous silicate MCM-41 and Ti(OBu^n)$_4$, Ti(OBu^n)$_3$(acac) or Ti(OBu^n)$_2$(acac)$_2$ titanium precursors by the cocondensation method. IR, ^{29}Si MAS NMR and N$_2$ sorption showed that titania existed as a thin layer on the channel surface of mesoporous silicate. Raman and solid state UV–VIS investigations revealed that the introduced titania were amorphous with tetrahedral coordination. Photodecomposition of phenol and photoreduction of Cr(VI) to Cr(III) were used as the models to test the photoactivity of the titania-modified MCM-41. Although the activity of titania-modified MCM-41 was not so high as nanosized crystalline anatase, they still exhibit reasonable photoactivities.

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