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Photocatalytic decomposition of 4-nitrophenol on Ti-containing MCM-41

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Abstract

A series of Ti-containing MCM-41 samples, such as Ti-MCM-41 with variable Si/Ti ratios and Cr–Ti-substituted TiO_2-loaded MCM-41 having different TiO_2 loading, were prepared and studied for the photocatalytic decomposition of 4-nitrophenol in UV and visible light. The samples were characterized using surface area measurement, XRD, FT-IR, and UV–vis DRS techniques. In the case of the Ti-MCM-41 samples with Si/Ti ratios higher than 20 which were found to have typical mesoporous structure, the framework incorporation of Ti into MCM-41 increased with decreasing Si/Ti ratio. On the contrary, the Ti-MCM-41 with lower Si/Ti ratio (Si/Ti = 10) shows low structural integrity and the formation of Ti-oxide species, leading to a considerable decrease in surface area. In the case of Cr–Ti-substituted TiO_2-loaded MCM-41 samples, significant absorption occurs in visible light and the absorption in both UV and visible region increases with increasing TiO_2 loading. However, when the amount of TiO_2 loaded on Cr–Ti-MCM-41 increased above 33 wt.%, the absorption in visible light increased slightly. Thus, it seems that, at higher TiO_2 loading, some TiO_2 particles are not closely bound to the wall of Cr–Ti-MCM-41. The photocatalytic activities of Ti-containing MCM-41 samples were strongly influenced by the amount of Ti. Under UV illumination, the highest photocatalytic activity for photocatalytic decomposition of 4-NP was observed for the Ti-MCM-41 having Si/Ti ratio of 20. Among various Ti-containing MCM-41 materials prepared in this work, only Cr–Ti-substituted TiO_2-loaded MCM-41 catalysts exhibited discernable photocatalytic activities in visible light, and their photocatalytic activities increased considerably with increasing TiO_2 loading up to 33 wt.%. Further increase in TiO_2 loading enhanced photocatalytic activity slightly.

Keywords: Ti-containing MCM-41; Photocatalytic decomposition; 4-Nitrophenol; UV and visible light

1. Introduction

Heterogeneous photocatalysis has drawn increased attention as a relatively new technique for pollution control. Among various metal oxide semiconductors, titania, especially anatase phase, has been proved to be one of the most efficient photocatalysts due to its chemical stability, relatively low price, non-toxicity and optical and electronic properties. Recently, mesoporous materials are of great interest to photocatalysis because of their large and uniform pore size, high surface area and long range ordering structure. One form of mesoporous materials, MCM-41, which exhibits a uniform hexagonal arrangement of cylindrical pores of diameter varying from 15 to 100 Å, has received great attention.

Siliceous MCM-41 has limited catalytic applications. Therefore, isomorphous substitution of silicon with a transition metal is necessary to obtain considerable catalytic activity. Recently, it has been reported that incorporation of photoactive elements into MCM-41 framework gives it unique photocatalytic reactivities [1,2]. In addition, it has been claimed that photocatalytic activity of TiO_2 increased when it was loaded on zeolite or mesoporous silica support [3]. Especially, TiO_2-loaded on transition-metal-substituted MCM-41 was found to have discernible photocatalytic activity under visible light irradiation [4]. However, the effect of the amount of Ti in Ti-containing MCM-41 materials on their photocatalytic activities is not clear.

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In this study, Ti-containing MCM-41 samples with variable Si/Ti ratios were prepared, and their photocatalytic properties were studied. In some case, another transition metal (Cr) besides Ti is also incorporated into MCM-41 structure and then TiO_2 is loaded on these materials with the aim of extending the photocatalytic activity toward the visible region. The 4-nitrophenol (4-NP), which is one of the most refractory pollutants present in industrial wastewater, was used as a probe organic compound for photodecomposition.

2. Experimental

2.1. Catalyst preparation and characterization

Ti-substituted MCM-41 materials with varying Si/Ti ratio in the range of 50–10 were synthesized by hydrothermal method [5] using tetraethyl orthosilicate (TEOS) and titanium isopropoxide (TIPO) as the sources of Si and Ti, respectively. Cr–Ti-substituted MCM-41 material with Si:Cr:Ti = 1:0.0125:0.025 was also synthesized as previously reported [4] using TEOS, TIPO, and chromium nitrate as metal sources. All samples were prepared in the presence of cetyltrimethyl ammonium bromide as a template. TiO_2-loaded Cr–Ti-MCM-41 photocatalysts were prepared by impregnating with an aqueous solution of TIPO and the range of TiO_2 loading was 23–38 wt.%. P-25 TiO_2 (Degussa) was used as a reference catalyst.

The BET surface areas of the catalysts were determined by physical adsorption of nitrogen at −196 °C in a Micro Meritics, Gemini III 2375. X-ray diffraction (XRD) analyses of the catalyst were carried out on a Philips X'pert diffractometer using Cu Kα radiation. UV–vis diffuse reflectance spectroscopy (DRS) was performed on Varian Cary 100 with PTFE (polytetrafluoroethylene) as standard. IR spectra of the catalysts were obtained using Jasco FT/IR-5300 for which the samples were diluted with KBr.

2.2. Photocatalytic experiments

The photocatalytic reactor consists of 500 mL annular Pyrex body with sampling port and gas inlet and outlet ports. The cooling water in a quartz cylindrical jacket round the lamp was used to keep the reaction temperature constant (30 ± 2 °C). Prior to illumination, the reaction suspension was stirred continuously in dark for 1 h to ensure adsorption/desorption equilibrium. The suspensions were illuminated by using a 500 W mercury or halogen lamp (500 W mercury and halogen lamps were used as UV and visible light sources, respectively). During the illumination, the suspension was magnetically stirred and bubbled with air. The concentration of catalyst was 1 g/L and the initial concentration of 4-NP was 0.726 mmol/L. Samples were taken out at given time intervals and filtered at 10 000 rpm with a Hanil Supra 21 K centrifuge. The analysis of concentration of 4-nitrophenol in filtered solution was performed by means of Shimadzu UV-240 spectrophotometer.

Table 1
Specific surface area of catalyst

Catalyst	Si/Ti ratio	TiO_2 loading (wt.%)	Surface area (m^2/g)
MCM-41	–	–	968
Ti-MCM-41	50	–	622
Ti-MCM-41	40	–	619
Ti-MCM-41	30	–	613
Ti-MCM-41	20	–	606
Ti-MCM-41	10	–	437
Cr–Ti-MCM-41	40[a]	–	773
TiO_2/Cr–Ti-MCM-41	40[a]	23	653
TiO_2/Cr–Ti-MCM-41	40[a]	28	649
TiO_2/Cr–Ti-MCM-41	40[a]	33	646
TiO_2/Cr–Ti-MCM-41	40[a]	38	567

[a] Si/Ti ratio in MCM-41 framework, loaded TiO_2 is not included.

3. Results and discussion

3.1. Characterization of catalyst

Table 1 presents the surface areas of the catalysts. The incorporation of transition metal ion in MCM-41 structure and TiO_2 loading result in a considerable decrease in surface area. This is probably due to decrease in the structural integrity and the presence of occluded TiO_2 in the pores of MCM-41.

The structural properties of the MCM-41 samples after transition metal incorporation and TiO_2 loading were characterized by XRD measurements. The results are shown in Figs. 1 and 2.

As shown in Fig. 1, the XRD patterns of Ti-MCM-41 having higher Si/Ti ratios are consistent with siliceous MCM-41 [6]. With increase of titanium content (decrease of Si/Ti ratio), the XRD patterns, especially higher order Bragg reflections, become poorly resolved and the XRD peaks are broaden, which could be attributed to decrease in the

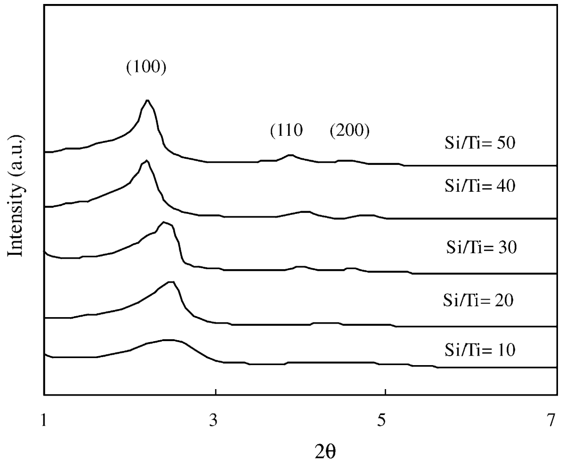

Fig. 1. X-ray diffraction patterns of Ti-MCM-41 with different Si/Ti ratios.

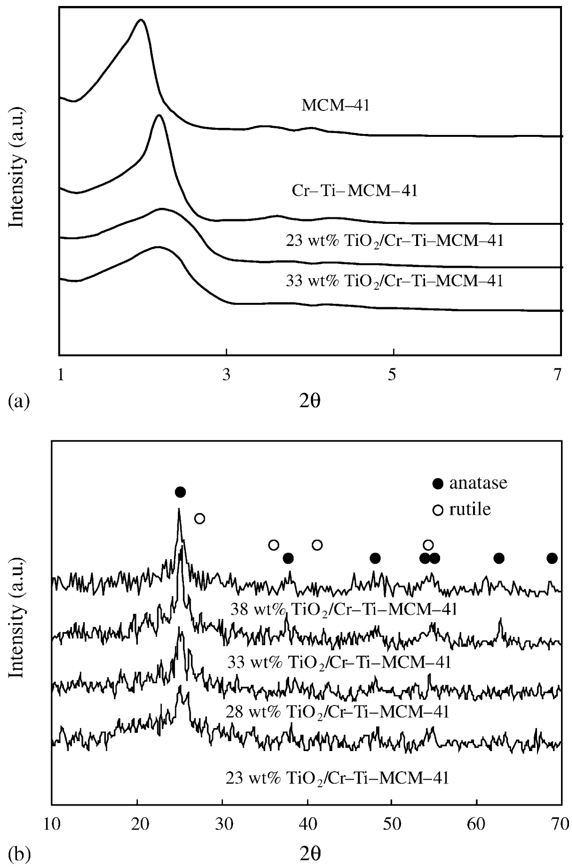

Fig. 2. X-ray diffraction patterns of Cr–Ti-substituted and TiO_2-loaded MCM-41 samples.

structural integrity. The intensity of (1 0 0) peak decreased with increasing Ti content and this may be due to the formation of non-framework metal oxide species inside the mesopores [7]. It is well known that incorporation of transition metal ions into the framework of pure silica polymorphs of zeolite is usually limited to less than 3 wt.% [8].

Above results strongly suggested that the Ti-MCM-41 with lower Si/Ti ratio (Si/Ti = 10) has low structural integrity and contains extra-framework Ti-oxide, which will be confirmed later by spectroscopic techniques.

It can be seen from Fig. 2(a) that the intensities and positions of (1 0 0) peak of the Cr–Ti-substituted and TiO_2-loaded samples are a little different from those of the siliceous MCM-41. The decrease in intensity of the peak and the shift of 2θ position to a higher value are probably resulted from slight structure change during chemical modification and TiO_2 loading [9]. For Cr–Ti-substituted TiO_2-loaded samples, the second part of XRD analysis was carried out in the range of 10–70° in order to assess the crystallinity of TiO_2. In the present work, the TiO_2 particles loaded on Cr–Ti-MCM-41 material seem to have mainly anatase structure, as can be seen in Fig. 2(b).

The IR spectra of the MCM-41 samples are presented in Figs. 3 and 4. For titanium-containing zeolites, the IR absorption at ~960 cm^{-1} commonly accepted as the characteristic vibration of Ti–O–Si. However, there are still some deputes over the assignment of the band at ~960 cm^{-1} in titanium-containing zeolites, which is often assigned to asymmetric Si–O–Ti vibration and is correlated with the presence of Si–OH group [2,10]. In present work, this band appeared in all spectra of MCM-41 samples even in the absence of Ti. Boccuti et al. [11] also discounted above assignment and interpreted their results in terms of the presence of Si–OH groups and Ti–O–Si bonds. Silanol groups are always present in Ti-free MCM-41.

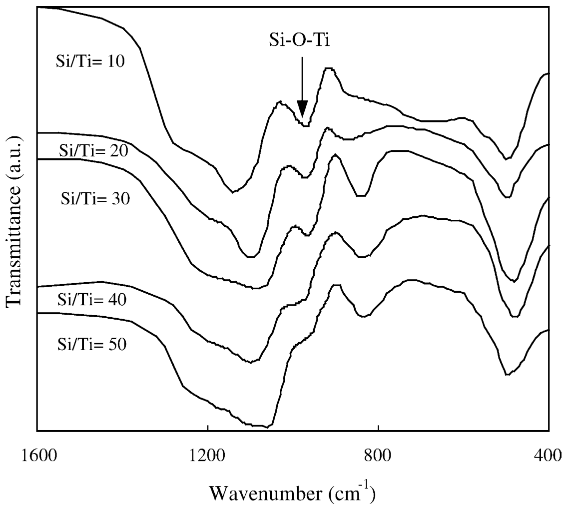

Fig. 3. IR spectra of Ti-MCM-41 with different Si/Ti ratios.

However, the band at ~960 cm^{-1} is rather weak in pure siliceous MCM-41 and this band increases in its intensity as Si/Ti ratio is decreased, as can be seen in Fig. 3. And systematic increase in intensity of IR absorption with increasing Ti content is generally taken as a proof of Ti incorporating into the framework of zeolite [6]. Thus, it seems that the incorporation of Ti(IV) into framework increases the asymmetry of local structure of MCM-41,

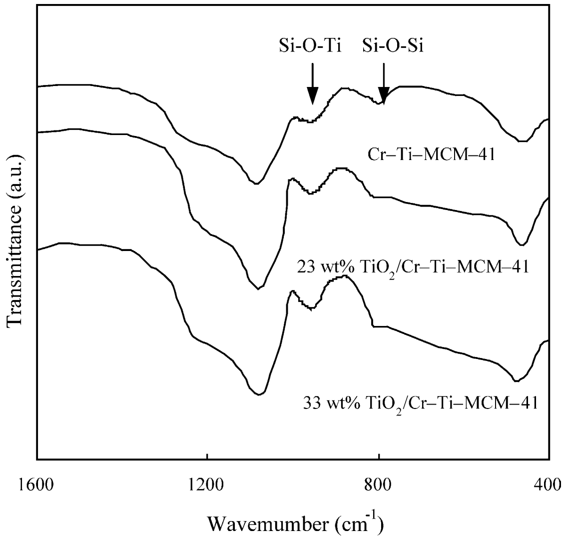

Fig. 4. IR spectra of Cr–Ti-substituted and TiO_2-loaded MCM-41 samples.

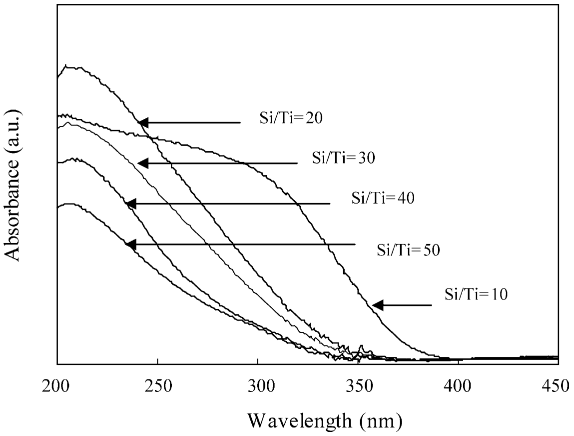

Fig. 5. UV–vis diffuse reflectance spectra of Ti-MCM-41 with different Si/Ti ratios.

which causes to increase the intensity of the band at ~960 cm^{-1}.

It was also reported that, when TiO_2 is loaded on MCM-41, the ratio of the area of the band at ~960 cm^{-1} (asymmetric Si–O–Ti vibration) to the band at ~800 cm^{-1} (symmetric Si–O–Si vibration) increases [2]. Similar results were observed in the present work. The IR spectra of the TiO_2-loaded Cr–Ti-MCM-41 in Fig. 4 revealed that the area of the band at ~960 cm^{-1} increases with increasing of TiO_2 loading, while that at ~800 cm^{-1} shows almost no discernible change.

UV–vis spectroscopy has been used widely for the characterization of the nature and coordination of Ti^{4+} ions in titanium-substituted molecular sieves [12,13]. The UV–vis diffuse reflectance spectra of the samples prepared in our study are given in Figs. 5 and 6. Without Ti ion, MCM-41 exhibited no absorption band above 220 nm.

The band near 220 nm is generally assigned to Ti in tetrahedral coordination, whereas the band at around 270 nm is assigned to Ti in octahedral coordination [1,14]. As can be seen in Fig. 5, the Ti-MCM-41 samples having Si/Ti ratio higher than 20, the intensity of the band at near 220 nm increases monotonically with increasing Ti content, indicating the increase of the framework incorporation of Ti into MCM-41. On the other hand, the band at around 330 nm assigned to Ti-oxide species becomes prominent when the Si/Ti ratio is 10. This can be attributed the presence of foreign ions with relatively high concentration in the gel during synthesis, which can hinder the structure-directing action of the template by changing the ionic strength of the medium [15], probably resulting in low structural integrity and the formation of Ti-oxide species.

As shown in Fig. 6(a), the behavior of visible light absorption of Cr–Ti-substituted TiO_2-loaded MCM-41 samples was drastically different from that of neat TiO_2 (P-25). Significant absorption occurs in visible light in TiO_2-loaded Cr–Ti-MCM-41 and the absorption in both UV and visible region increases with increasing TiO_2 loading. However, when the amount of TiO_2-loaded on Cr–Ti-MCM-41 increased above 33 wt.%, the absorption in visible light increased slightly and the spectrum of 38 wt.% TiO_2-loaded sample was almost identical to that of 33 wt.% TiO_2-loaded sample. Therefore, it seems that, at higher TiO_2 loading, some TiO_2 particles are not closely bound to the wall of Cr–Ti-MCM-41 since the light absorption of TiO_2-loaded Cr–Ti-MCM-41 in visible region arises primarily due to the charge generation happening at the heterojunction of loaded titania with Cr-incorporated MCM-41 [4]. These results suggest that above materials can be potentially good candidates for the photocatalyst capable of working in visible light.

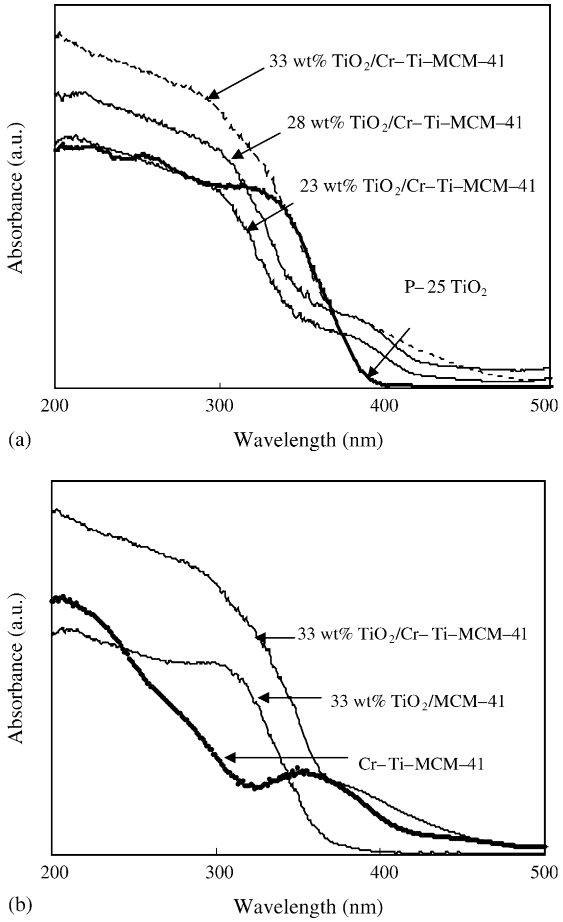

Fig. 6. UV–vis diffuse reflectance spectra of neat TiO_2, Cr–Ti-substituted and TiO_2-loaded MCM-41 samples.

The absorption of light below 350 nm in TiO_2-loaded Cr–Ti-MCM-41 is similar to that of titania. Then absorption by TiO_2 itself sharply decreased, and absorption of light in the range of 350–500 nm can be ascribed to the heterojunction of TiO_2 with the corresponding transition metal incorporated in MCM-41 [12]. This fact can be seen more clearly in Fig. 6(b). TiO_2-loaded Cr–Ti-MCM-41 revealed the absorption of light above 400 nm, while TiO_2-loaded MCM-41 showed no absorption band in this range. Cr–Ti-MCM-41 showed distinct bands at around 220 and 360 nm, and the latter may be due to Cr-oxide moieties [16].

In addition, it can be seen that a decrease in TiO_2 loading causes a shift in the absorption band of TiO_2 toward short wavelength regions. This may be attributed to the well-

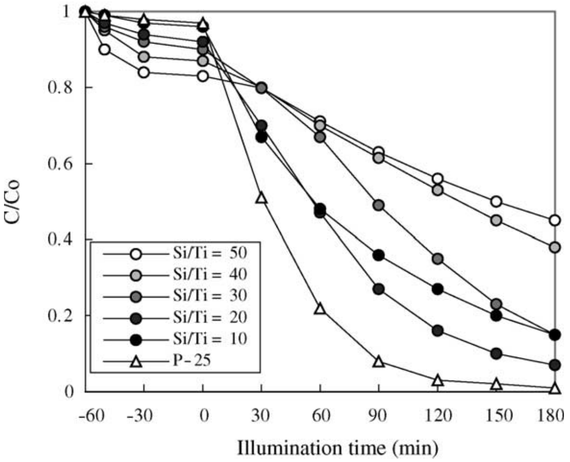

Fig. 7. Photocatalytic decomposition of 4-NP over Ti-MCM-41 with different Si/Ti ratios and P-25 TiO_2 catalysts in UV.

known size quantization effect arising from the presence of extremely small titanium oxide particles [17], since TiO_2 particles loaded on Cr–Ti-MCM-41 material are found to be nanocrystalline and the crystallite size of TiO_2 nanoparticle decreased with decreasing TiO_2 loading (Fig. 2).

3.2. Photocatalytic decomposition of 4-NP under UV illumination

Fig. 7 shows photocatalytic decomposition of 4-NP over Ti-MCM-41 under UV illumination. In the absence of catalyst or UV illumination, almost no decomposition of 4-NP was observed.

As can be seen in Fig. 7, the photocatalytic activity of Ti-MCM-41 increased with decreasing Si/Ti ratio. It was demonstrated that the process of photocatalytic decomposition of 4-NP exhibited apparent first order kinetics, expressed by the simplified equation [18,19]:

$$\ln(C_0/C) = k't \qquad (1)$$

The data in Fig. 7 were fitted to the corresponding logarithmic expression to get an apparent rate constant, k'. Although this rate constant is not regarded as fully interpretable, the k' simply serves to compare relative activities of the catalysts under study. Table 2 lists the values of k' over transition metal-substituted and TiO_2-loaded MCM-41 catalysts and TiO_2.

The reaction rate for photocatalytic decomposition of 4-NP over Ti-MCM-41 reached a maximum at Si/Ti ratio of 20. Further decrease in Si/Ti ratio caused a decrease in reaction rate, which is likely attributed to the low structural integrity and the presence of Ti-oxide species, as observed in XRD patterns and UV–vis spectra.

It seems that all Ti atoms in Ti-MCM-41 having Si/Ti ratio higher than 20 are incorporated into framework and act as photocatalytic active sites. It was reported that bulk TiO_2 and framework titanium incorporated within zeolite showed different activities in various photocatalytic reactions [20–22]. The results in Fig. 7 obtained by using the same catalyst loading (1 g/L) show that TiO_2 (P-25) has a higher reaction rate per gram of catalyst than the Ti-MCM-41 catalyst having Si/Ti ratio of 20. However, if we compare the titanium content in Ti-MCM-41 with that in TiO_2, it can be thought that the titanium in Ti-MCM-41 framework acts as a more active photocatalytic site than that in TiO_2 (P-25) since the amount of titanium is much lower in the Ti-MCM-41 compared to P25 TiO_2 catalyst. It may be due to higher dispersion of Ti in MCM-41 structure as compared with bulk TiO_2.

Table 2
Rate constants for 4-nitrophenol decomposition over various transition metal-substituted and TiO_2-loaded MCM-41 catalysts and TiO_2 under UV and visible light illumination

Catalyst	k' (min^{-1}), UV	k' (min^{-1}), visible light
Ti-MCM-41 (Si/Ti = 50)	0.003	–
Ti-MCM-41 (Si/Ti = 40)	0.004	–
Ti-MCM-41 (Si/Ti = 30)	0.009	–
Ti-MCM-41 (Si/Ti = 20)	0.014	–
Ti-MCM-41 (Si/Ti = 10)	0.011	–
TiO_2	0.026	Nil
23 wt.% TiO_2/Cr–Ti-MCM-41	–	0.0005
28 wt.% TiO_2/Cr–Ti-MCM-41	–	0.0015
33 wt.% TiO_2/Cr–Ti-MCM-41	–	0.0026
38 wt.% TiO_2/Cr–Ti-MCM-41	–	0.0031

3.3. Photocatalytic decomposition of 4-NP under visible light illumination

Among various Ti-containing MCM-41 materials prepared in this work, only Cr–Ti-substituted TiO_2-loaded MCM-41 catalyst exhibited a considerable photocatalytic activity in visible light. It was previously reported that, among various transition metal (Cr, V, Fe)-substituted titania-loaded MCM-41 materials, the chromium substituted MCM-41 was found to serve as the best support for titania to achieve the highest degradation rates of formic acid and 2,4,6-trichlorophenol in visible light [4]. It was also demonstrated that Cr-incorporated MCM-41 is effective for the photoreduction of NO in visible light [16].

It was claimed that enhanced absorption of visible light is a necessary condition for the photocatalyst capable of working in visible light, but not a sufficient condition for its ability to perform photocatalytic reaction at a measurable rate under visible light [4]. As can be seen from Fig. 6(b), neat Cr–Ti-MCM-41 showed some absorption in visible light region. However, the catalyst without loading of TiO_2 (neat Cr–Ti-MCM-41) yields no discernible activity in visible light.

The time course of the photodecomposition of 4-NP on irradiated catalyst is shown in Fig. 8.

P-25 TiO_2 revealed high photocatalytic activity under UV irradiation, while it showed almost no considerable reaction rate in visible light. Cr–Ti-MCM-41 samples loaded with TiO_2 exhibited some activity in both UV and visible light,

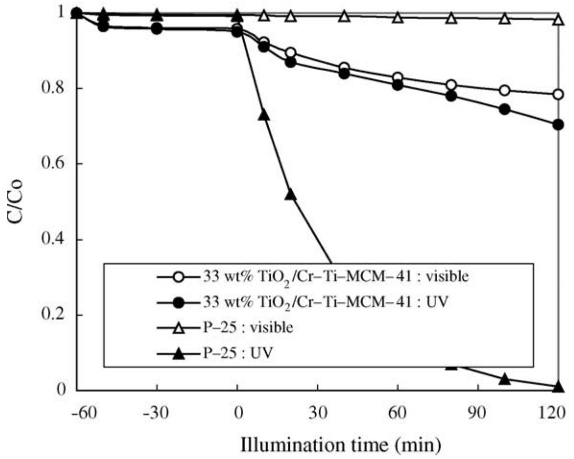

Fig. 8. Effect of TiO_2 loading on the photocatalytic decomposition of 4-NP over TiO_2/Cr–Ti-MCM-41 catalysts in visible light.

and the reaction rate in UV was a little higher than that in visible light. These results suggest that the titanium in unloaded TiO_2 acts as active site only in UV, while the titanium in TiO_2-loaded over Cr–Ti-MCM-41 act as active site in both UV and visible light.

Fig. 9 presents the photocatalytic decomposition of 4-NP over TiO_2/Cr–Ti-MCM-41 catalysts having various TiO_2 loading in visible light.

As mentioned above, the catalyst without loading of TiO_2 (neat Cr–Ti-MCM-41) was tested for the photodecomposition of 4-NP in visible light (not shown) and yields no discernible activity. On the contrary, Cr–Ti-MCM-41 samples loaded with TiO_2 exhibited photocatalytic activity. The photocatalytic activity of TiO_2/Cr–Ti-MCM-41 increased steadily with increasing TiO_2 loading up to 33 wt.%. Further increase in TiO_2 loading enhanced photocatalytic activity slightly. This may be due to the fact that the interaction of loaded TiO_2 with Cr-incorporated MCM-41 is primarily responsible for the photocatalytic activity of TiO_2/Cr–Ti-MCM-41 in visible light and, in the case of higher loading, all TiO_2 particles cannot interact closely with Cr. Above results are correlate well with the observation in UV–vis DRS spectra (Fig. 6(a)) in which the absorption of visible light by TiO_2/Cr–Ti-MCM-41 shows discernable increase with increasing TiO_2 loading up to 33 wt.%.

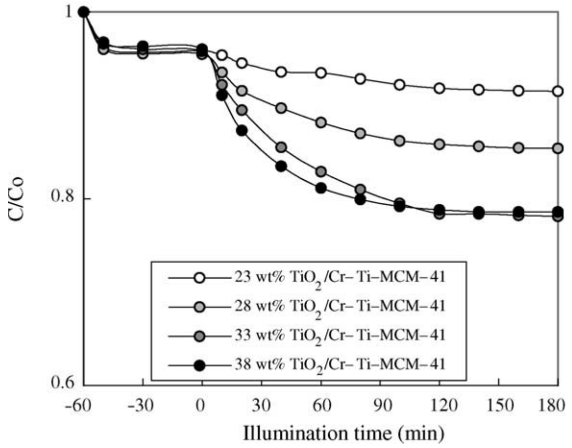

Fig. 9. Photocatalytic decomposition of 4-NP over TiO_2/Cr–Ti-MCM-41 catalysts in visible light.

4. Conclusions

For higher Si/Ti ratios (Si/Ti $\geq$ 20), Ti-MCM-41 samples have typical mesoporous structures and the framework incorporation of Ti into MCM-41 increased with decreasing Si/Ti ratio. On the contrary, the Ti-MCM-41 with lower Si/Ti ratio (Si/Ti = 10) shows low structural integrity and the formation of Ti-oxide species, leading to considerable decrease in surface area. For Cr–Ti-substituted TiO_2-loaded MCM-41 samples, significant absorption occurs in visible light and the absorption in both UV and visible region increases with increasing TiO_2 loading. However, when the amount of TiO_2-loaded on Cr–Ti-MCM-41 increased above 33 wt.%, the absorption in visible light increased slightly. Thus, it seems that, at higher TiO_2 loading (>33 wt.%), some TiO_2 particles are not closely bound to the wall of Cr–Ti-MCM-41. The photocatalytic activities of Ti-containing MCM-41 samples were strongly influenced by the amount of Ti. From the results of photocatalytic decomposition of 4-NP over Ti-MCM-41 in UV, it was found that the photocatalytic activity of Ti-MCM-41 increased with decreasing Si/Ti ratio and reached a maximum at Si/Ti ratio of 20. The higher photocatalytic activity of Ti-MCM-41 may be due to higher dispersion of Ti in MCM-41 structure as compared with bulk TiO_2. Among various Ti-containing MCM-41 materials employed in the present work, only Cr–Ti-substituted TiO_2-loaded MCM-41 materials exhibited discernable photocatalytic activities in visible light. The photocatalytic activity of Cr–Ti-MCM-41 for decomposition of 4-NP in visible light increased considerably with increasing TiO_2 loading up to 33 wt.%. Further increase in TiO_2 loading enhanced photocatalytic activity slightly.

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