



Effects of SiO₂ and Pt on photocatalytic activity of TiO₂ for decomposition of monochlorobenzen

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ABSTRACT

In recent years much attention has been focused on photocatalytic degradation of organic pollutants by TiO₂ particles irradiated by ultraviolet (UV) light. This method is undoubtedly an effective approach toward abatement of a wide variety of harmful/toxic organic pollutants in wastewaters. Unfortunately, the need of an ultraviolet excitation source restricts its technological utility to limited applications. In this work, TiO₂/SiO₂ and Pt-TiO₂/SiO₂ nanoparticles were prepared in anatase form to improve and modify TiO₂ photocatalytic activity in UV and visible light. In the case of using SiO₂ the results showed that the crystal size and surface area of TiO₂ have been improved from 17 to 5 (nm) and 80 to 555 (m²/g) respectively. In the case of using platinum (Pt), platinum can be either doped in the crystalline structure of TiO₂/SiO₂ or deposited on the surface of TiO₂/SiO₂. The results showed that photocatalytic activity of Pt-TiO₂/SiO₂ and TiO₂/SiO₂ has been increased in visible and UV light respectively. The characterizations of catalysts were performed by XRD, FTIR, SEM, TEM, BET and UV-Vis diffuse reflectance spectra. Finally, in order to assess photocatalytic activities of TiO₂/SiO₂ and Pt-TiO₂/SiO₂, degradation of monochlorobenzene (MCB) was tested under UV and visible light. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Nanophotocatalyst;
TiO₂/SiO₂;
Platinum (Pt);
Monochlorobenzen (MCB);
UV light;
Visible light.

INTRODUCTION

Nowadays due to industrial growth, the environmental pollution has been increased and attained to a dangerous level in developing/developed countries. In order to decrease environmental pollutants, photooxidation process by using TiO₂ photocatalyst is being widely studied as a relatively new technique of pollution abatement^[1-3]. TiO₂ semiconductor fine nanoparticles are ideal and powerful photocatalysts due to their

chemical stability, non toxicity and high reactivity for the elimination of pollutants in air and water. However, TiO₂ semiconductors have a relatively large band gap of 3.2 eV, corresponding to wavelengths shorter than 388 nm. Unfortunately, the need of an ultraviolet (UV) excitation source restricts its technological utility for limited applications. For widespread applications, effective TiO₂ photocatalyst in visible radiation or solar light needs to be developed as future generation photocatalytic material. TiO₂ absorbs only 3-5% of the solar spec-

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trum energy, so in order to enhance the photocatalytic activity of TiO₂, modification of its surface properties; crystalline structure and composition are needed^[4-9]. For example the surface modification by doping transition metals such as Platinum (Pt) and controlling nanoparticles size have been employed to extend the light absorption in the visible (bathochromic shift of the band gap energy) or UV region^[10-14]. Many methods have been developed to control the size of nanoparticles such as Langmuir and Blodgett films method^[15], Vesicles method^[16], reverse microemulsions method^[17] and surface active supports method^[18]. For example, Anderson and Bonard^[19] reported the effect of incorporation of silica on the TiO₂ particle size which increases the titania based photocatalyst activity in the UV light. According to their result for decomposition of Rhodamine-6G, the titania/silica mixed oxide (TiO₂/SiO₂) with the ratio of 30/70 produces the highest activity about three times higher than Degussa P25 titania.

In order to modify nanoparticle surface, addition of metal particles such as platinum, silver and ferrous on photocatalyst surface increases the light absorption efficiency and photocatalytic activity in the UV light^[20-23], while by doping these metals into the structure of semiconductors, their photocatalytic activity increase in the visible light. These increment of activities have been explained either by the suppression of hole-electron recombination or the electron trapping by the metals^[24]. It has been observed that the most active metal for photocatalytic enhancement is platinum, which can produce the highest Schottky barrier among the metals that facilitate electron capture^[25].

In this paper and in the first step, TiO₂ photocatalyst was synthesized by the sol gel method with precipitation of inorganic precursor (TiCl₄). Then effects of platinum and silica addition on photocatalytic activity of TiO₂ were investigated in the ultraviolet and visible lights. It should be mentioned that in the case of using platinum, platinum either can be deposited on the surface of TiO₂/SiO₂ (type A) or doped into the crystalline structure of TiO₂/SiO₂ (type B). In addition, in order to assess and compare the photocatalytic activity of TiO₂, decomposition of monochlorobenzene under ultraviolet and visible lights was studied. It should be mentioned that many researchers have studied photocatalytic degradation of organic compounds in the presence of TiO₂

under ultraviolet irradiation. For example Almquist et al. have reported MCB oxidation at temperature < 300 °C using V₂O₅/TiO₂ nanocatalyst without irradiation^[26]. They founded that MCB is stable in the presence of V₂O₅/TiO₂ at temperature up to 300 °C and they observed stable organic byproducts of MCB oxidation at temperature < 400 °C.

EXPERIMENTAL DETAILS

Materials and methods

In order to prepare different catalysts which synthesized in this work, the following materials were used: Tetra chloride titanium (TiCl₄, M=189.79), tetraethylortosilicate (Si(OC₂H₅)₄, M=208.33), Nitric Acid (HNO₃, M=63), Ammonia (NH₃, M=17), potassium hydroxide (KOH=56) and platinum chloride acid (H₂PtCl₆.6H₂O, M=517.92).

Preparation of TiO₂ and TiO₂/SiO₂ photocatalysts

Anatase TiO₂ and TiO₂/SiO₂ nanocrystalline powders were prepared by sol gel method. A certain amount of deionized water was added to TiCl₄ as starting material to form a suspension. Then an exact amount of HNO₃ ([H⁺]/[Ti⁺] = 0.5) was added to 500 ml of the suspension which contains 12 moles of titanium with strong stirring for about 7 hours. As a result, a stable titanium oxide sol has been formed. In the next step appropriate amount of tetraethylortosilicate (TEOS) was dropped into the previous titanium oxide sol until the desired ratio of TiO₂/SiO₂ = 30/70 (mole ratio) obtain. Then the sol was dried and calcined for 3 hours to obtain TiO₂/SiO₂ catalyst.

Pt modified TiO₂/SiO₂ catalyst

1% Pt-TiO₂/SiO₂ photocatalyst was prepared by photo deposition method similar to the Kraeutler and Bard method^[27]. All preparation experiments were carried out in a fluidized bed photo reactor consists of 250 ml cylindrical quartz body with sampling and gas inlet/outlet ports. The prepared TiO₂/SiO₂ powder in section (2.2) and aqueous platinum chloride acid (H₂PtCl₆.6H₂O) were added into 100 ml of distilled water with vigorous stirring to produce basic suspension. The pH of this suspension was adjusted to 6.8-7 by addition of 0.1 N potassium hydroxide (KOH) solution.

In the next step in order to produce type (A) of Pt-TiO₂/SiO₂ (TiO₂/SiO₂ with Pt on its surface), the basic suspension was stirred by pure nitrogen gas flow up to 30 min. Then this suspension irradiated with UV light (250W) for photodeposition of Pt on TiO₂/SiO₂ surface. In order to produce type (B) (dopped Pt in TiO₂/SiO₂ structure), the basic suspension was stirred by pure nitrogen gas flow and irradiated by UV light simultaneously until color of the suspension gradually turned from yellow to gray. Finally the result solutions (type (A) and type (B)) which contain Pt-TiO₂/SiO₂ catalyst were centrifuged and washed with distilled water until no chlorine was detected in rinsing water and dried overnight at about 383 K. The ICP analysis indicates that platinum presence in type (A) and type (B) catalysts is about 18% and 80% respectively.

Characterization of nano photocatalysis

The crystalline structure of nano photocatalysts was assessed and characterized by X-ray diffractometry (D4-BRUKER and Cu-K α radiation at 30 kV and 20 mA). The chemical structure of prepared particles was examined using Fourier transform infrared spectrophotometer (FTIR, SHIMADZU-840S). The diffuse reflectance UV-Vis absorption spectra of catalysts were recorded by UV-Vis spectrophotometer (Shimadzu-2550). In addition, the particles morphology was observed by Scanning Electron Microscopy (SEM, Philips – XLF30) and Transition Electron Microscopy (TEM, CM200FEG). Surface area was calculated using nitrogen absorption data at 298 K and BET analysis (MICRO MERITICS-GEMINI)

Photocatalytic experiment

In order to determine activity of each of the four catalysts (TiO₂, TiO₂/SiO₂ and Pt-TiO₂/SiO₂: type (A) and (B)) degradation of Monochlorobenzene (MCB) in a quartz tube batch reactor was investigated. In each experiment, 0.2, 0.25 and 0.3 grams of each catalyst was dissolved in 200 ml of MCB (300 ppm) solution in water. Before irradiation, the mixtures were maintained in darkness with stirring for one hour. At given irradiation time intervals, 5 ml of each solution was taken and analyzed by means of a UV-Vis spectrophotometer (Shimadzu PC1201, maximum absorbance was taken at 627 nm). Also all experiments repeated in different

pH (pH=3, 5 and 6). The obtained results show that the 0.25 grams of TiO₂/SiO₂ and Pt-TiO₂/SiO₂ (type (B)) catalysts at pH=3 are the best condition for degradation of monochlorobenzene at temperature <40°C under UV and visible light respectively.

RESULTS AND DISCUSSIONS

XRD analysis

The XRD patterns of TiO₂ and TiO₂/SiO₂ nano powders showed five clear diffraction peaks at 25.48°, 38.24°, 48.12°, 54.96° and 63.48° (Figure 1). All peak which indexed as (101), (004), (200), (105) and (204) diffraction lines in the XRD pattern was assigned to anatase phase of TiO₂ (ICCD card File No 21-1272). It should be noted that there is a character of residual amorphous SiO₂ in the XRD pattern. This means that the materials consist of TiO₂ nanocrystals and SiO₂ based powder. The size of nanoparticles can be calculated by Scherrer's equation. By using this equation the crystal size of TiO₂ and TiO₂/SiO₂ were estimated 17 and 5 nm respectively while the surface area was 80 and 555 m²/g respectively.

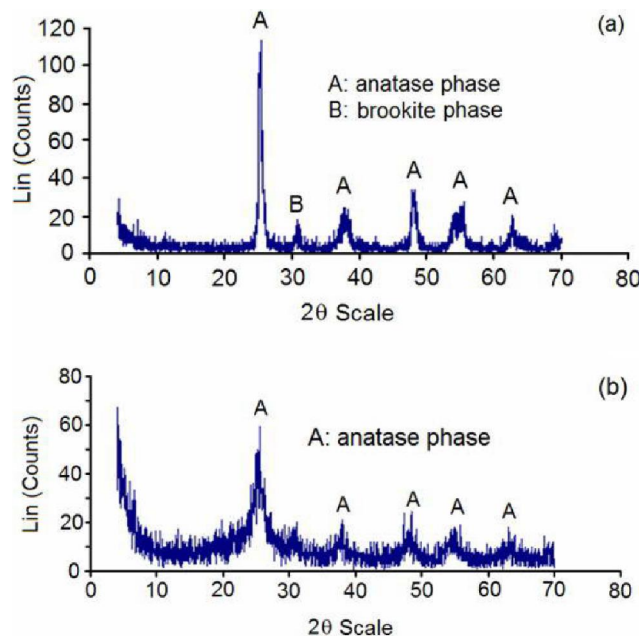


Figure 1 : The XRD patterns of TiO₂ (a) and TiO₂/SiO₂ (b) nano powders

Figure 2 shows the X-ray diffraction pattern of Pt-TiO₂/SiO₂ photocatalyst in both types (A) and (B). As it can be seen, in type (A), the platinum peak has occurred

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at $2\theta=40^\circ$ corresponding to ASTM (23-1306 card), whereas there is no distinct peak for platinum in type (B). In fact, in type (A), because of existence of oxygen on the surface of TiO₂/SiO₂, platinum can not doped into crystalline network but can deposit on the surface of TiO₂/

SiO₂, thus the platinum peak observed in the XRD pattern. But in type (B), continuous pure nitrogen gas flow causes platinum penetrate into crystalline network instead of titanium. Therefore, there is not distinguished platinum peak in the X-ray diffraction pattern of type (B).

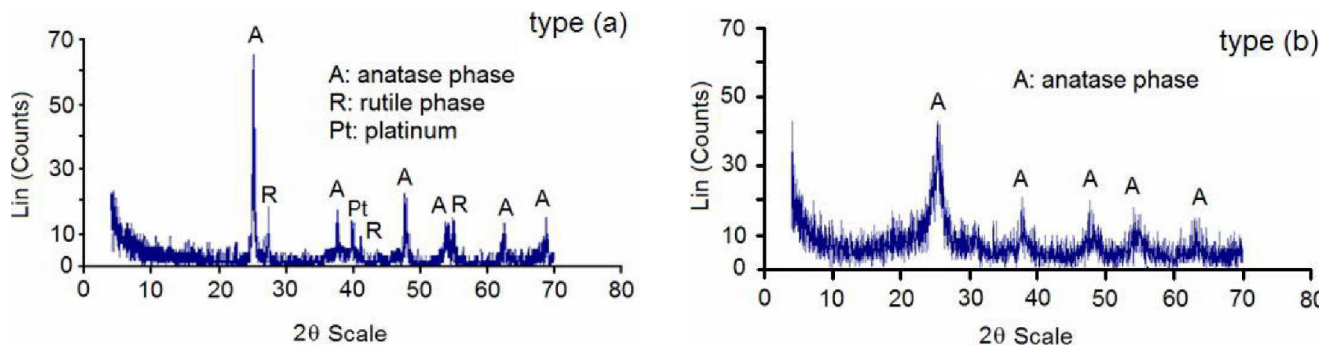


Figure 2 : The x-ray diffraction pattern of Pt-TiO₂/SiO₂ photocatalyst in both types (A) and (B).

FT-IR analysis

The FT-IR spectra of TiO₂ and TiO₂/SiO₂ nanoparticles have been shown in Figures 3 and 4 respectively. The observed peaks at 1070, 950 and 460 cm⁻¹ indicate the bands of (Si--O--Si) asymmetric stretching near 1070 cm⁻¹, (Ti--O--Si) asymmetric stretching around 950 cm⁻¹ and (Ti--O) stretching near 460 cm⁻¹. In addition, the absorption band at about

950 cm⁻¹ is associated with titanium in four-fold coordination with oxygen in the SiO₄⁴⁻ structure. The broad absorption peak appearing near 3400 cm⁻¹ relates to stretching vibration of (Ti--OH) group. Also at 1620 cm⁻¹ region, a band assigned to water appears. It should be noted that the intensities of absorption peaks due to OH group near 1620 and 3400 cm⁻¹ increased with increasing of silica amount.

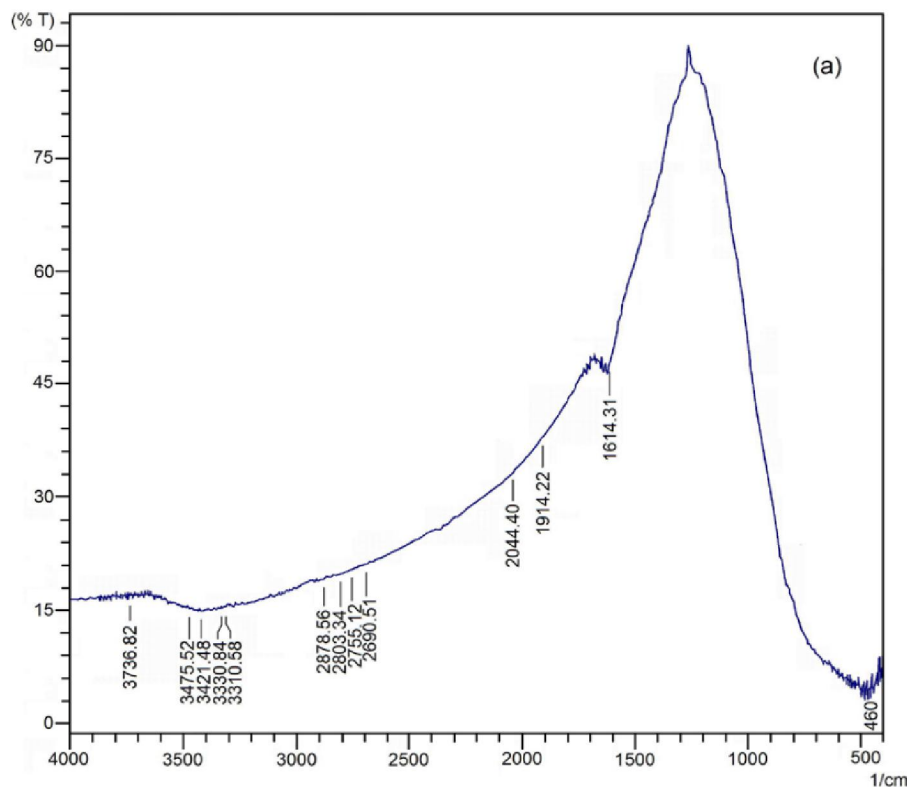


Figure 3 : The FT-IR spectra of TiO₂ nanoparticles

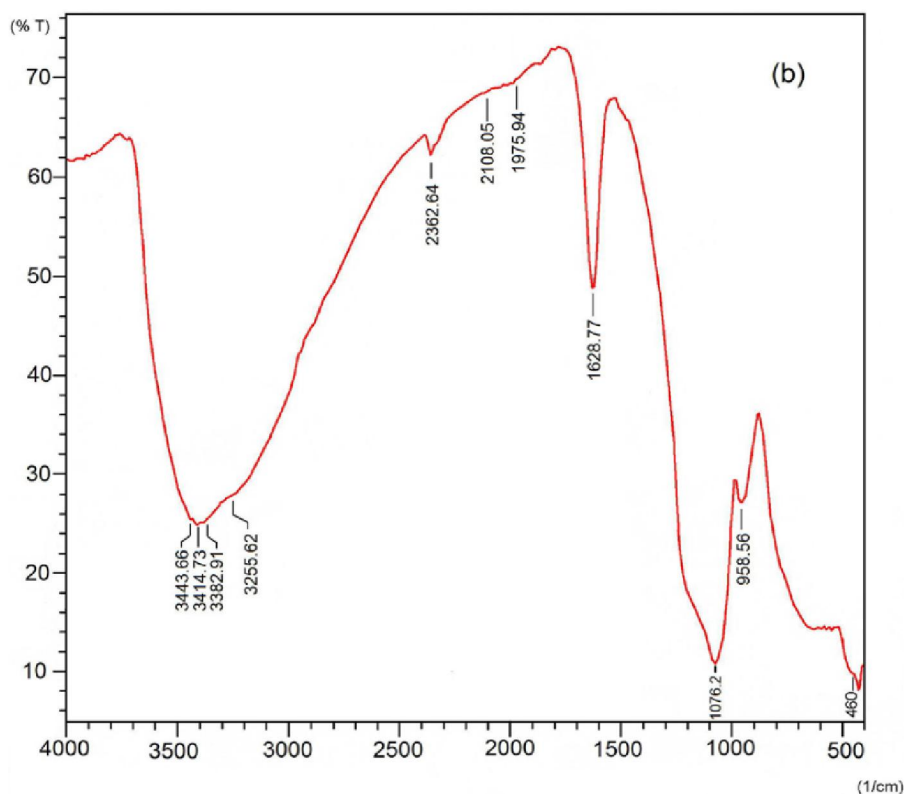


Figure 4 : The FT-IR spectra of $\text{TiO}_2/\text{SiO}_2$ nanoparticles

UV-Vis diffuses reflection spectra (DRS)

Figure 5 shows diffuse reflection spectra of TiO_2 and $\text{TiO}_2/\text{SiO}_2$ photocatalysts. As it can be observed the absorption band of $\text{TiO}_2/\text{SiO}_2$ exhibits partial hypsochromic shifts, which indicates the enhancement of photocatalytic activity of $\text{TiO}_2/\text{SiO}_2$ catalyst in UV light. This result indicates that the addition of SiO_2 in titania particles decreases crystal size and crystallinity by inhibiting the growth of the titania particles in crystalline network. The diffuse reflection spectra of TiO_2 and Pt- $\text{TiO}_2/\text{SiO}_2$ (type (A)) and TiO_2 and Pt- $\text{TiO}_2/\text{SiO}_2$ (type (B)) have been shown in figure 6 and 7 respectively. In figure 6, the absorption spectra of TiO_2 photocatalyst in comparison with the absorption spectra of Pt- $\text{TiO}_2/\text{SiO}_2$ type (A) shows partial hypsochromic shift which indicates platinum has been deposited on the surface of TiO_2 . But in figure 7 the absorption spectra of $\text{TiO}_2/\text{SiO}_2$ (type (B)) in comparison with the absorption spectra of TiO_2 shows distinguished batho-chromic shift which confirms platinum has been doped in the crystalline network of TiO_2 .

Scanning electron microscopy (SEM)

Morphological properties of TiO_2 and $\text{TiO}_2/\text{SiO}_2$

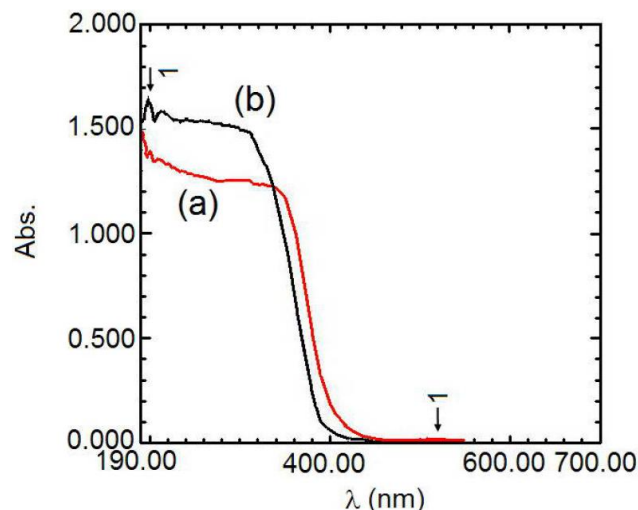


Figure 5 : The diffuse reflection spectra of TiO_2 (a) and $\text{TiO}_2/\text{SiO}_2$ (b) nanophotocatalysts

catalysts were investigated by Scanning Electron Microscopy (SEM). Figure 8 shows the multiangular and different sizes of nanocrystalline particles of TiO_2 catalyst, whereas in figure 9 because of existence of silica, nanocrystalline particles have spherical shape and distributed uniformly on the surface of $\text{TiO}_2/\text{SiO}_2$ catalyst. In addition, EDX analysis (Figure 10) of unloaded catalyst shows that the mean weight percentage of TiO_2 and

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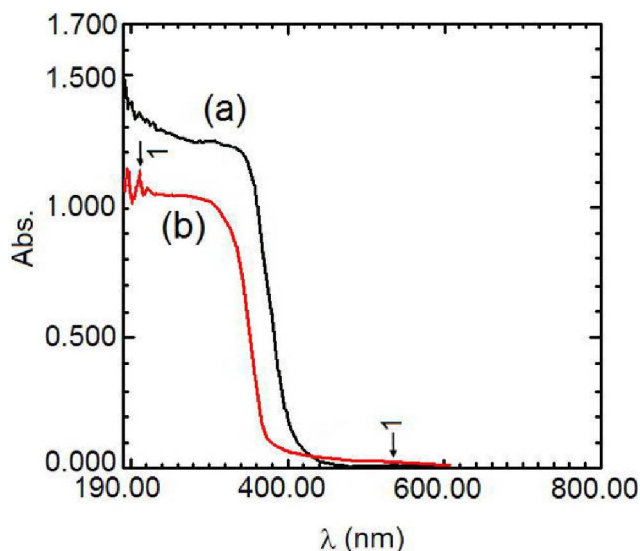


Figure 6 : The diffuse reflection spectra of TiO₂ (a) and type (A) of Pt-TiO₂/SiO₂ (b) nanophotocatalysts

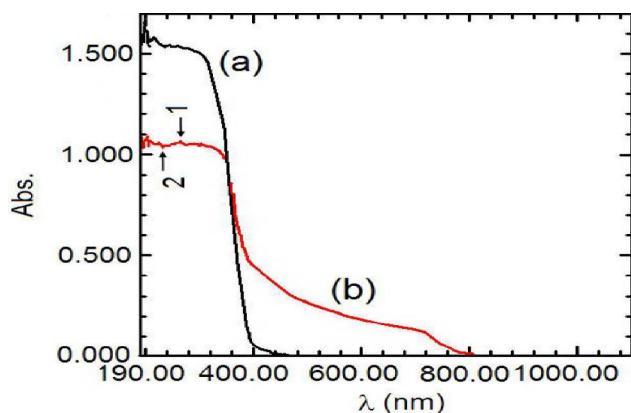


Figure 7 : The diffuse reflection spectra of TiO₂ (a) and type (B) of Pt-TiO₂/SiO₂ (b) nanophotocatalysts

SiO₂ are 27.7 and 72.3 respectively and the atomic percentage of TiO₂ and SiO₂ are 22.4 and 77.6 respectively.

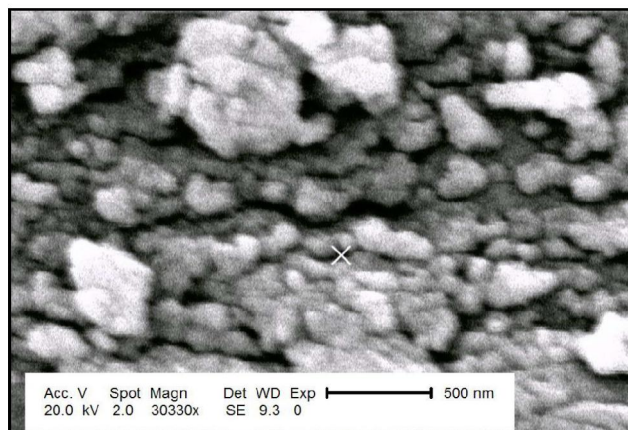


Figure 8 : The SEM image of TiO₂ nanophotocatalyst

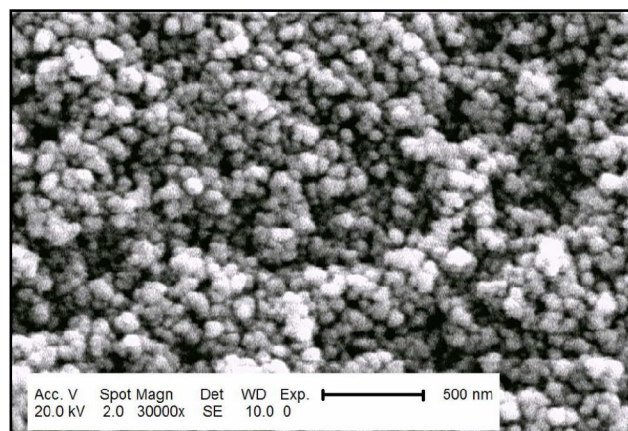


Figure 9 : The SEM image of TiO₂/SiO₂ nanophotocatalyst

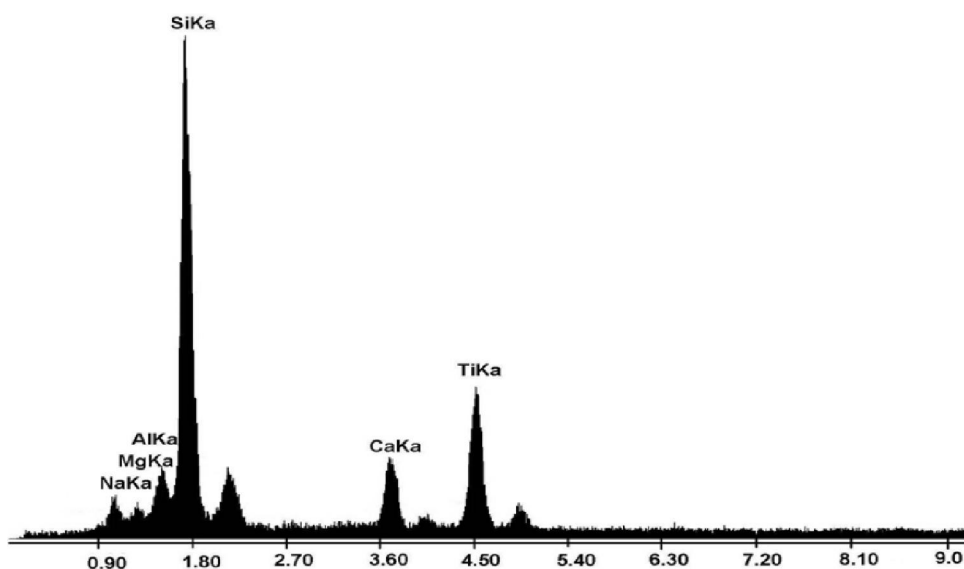


Figure 10 : The EDX analysis of TiO₂/SiO₂ nanophotocatalyst

Transition electron microscopy (TEM)

Figure 11 shows the TEM image of type (B) Pt-TiO₂/SiO₂. It can be observed that the platinum particles have spherical shape and their dispersions are uniform on surface of TiO₂/SiO₂. Also EDX analysis of this catalyst indicates existence of Pt, Si and Ti elements in crystalline network (Figure 12).

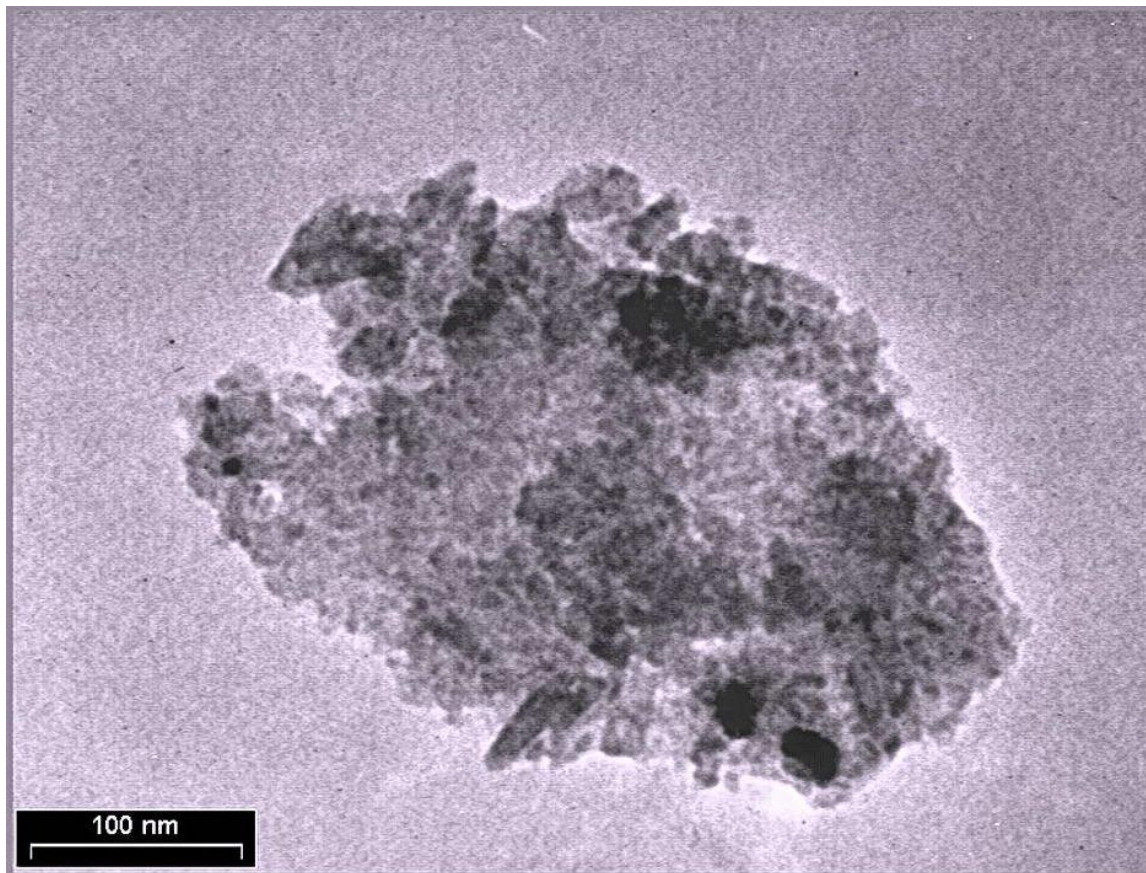


Figure 11 : The TEM image of type (B) Pt-TiO₂/SiO₂ nanophotocatalyst

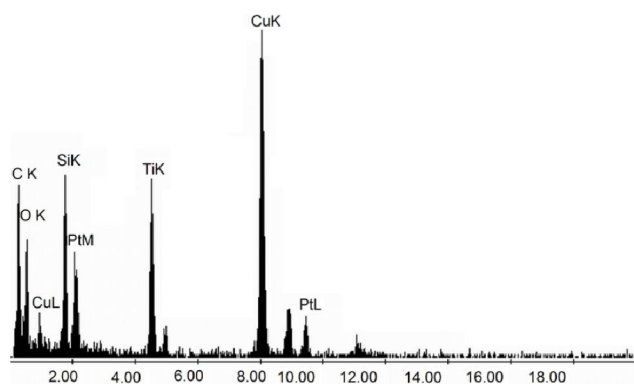


Figure 12 : The EDX analysis of Pt-TiO₂/SiO₂ type (B) nanophotocatalyst

degradation reaction on TiO₂/SiO₂ performs in a shorter time (90 min) in comparison with TiO₂ catalyst (240 min). In

Photocatalytic activity

In order to assess photocatalytic activity of prepared catalysts, degradation of Monochlorobenzene (MCB) with illumination of ultraviolet and visible light was investigated. Figures 13 and 14 show abatement performances of TiO₂ and TiO₂/SiO₂ catalysts on MCB degradation under UV light. As it can be seen, degra-

addition, abatement performances of TiO₂/SiO₂ and Pt-TiO₂/SiO₂ (type (B)) catalysts on MCB degradation under visible light have been shown in figures 15 and 16 respectively. As it can be observed absorption peaks of MCB have been diminished and disappeared by using type (B) Pt-TiO₂/SiO₂ photocatalyst after 90 min, whereas absorption peaks of MCB have no changes by using TiO₂/SiO₂. It should be mentioned that partial changes which observed in the absorption intensity of MCB in initial times (in figure 15), causes by the adsorption of MCB on the surface of TiO₂/SiO₂. Figure 17 shows the GC analysis of MCB extracted by CH₂Cl₂. As it can be observed, there are not any intermediates or byproducts after 90 min irradiation by type

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(B) Pt-TiO₂/SiO₂ under visible light.

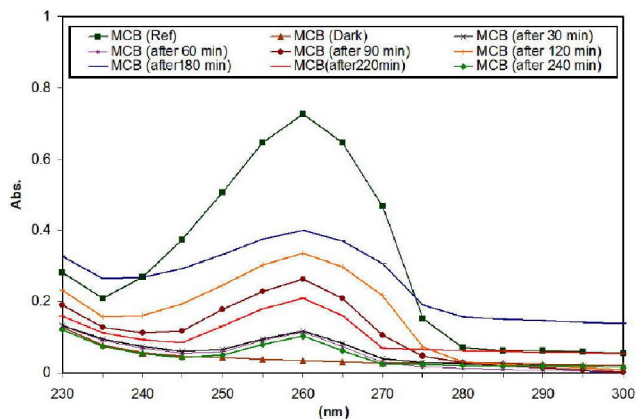


Figure 13 : Abatement performance of TiO₂ catalyst on MCB degradation under UV light

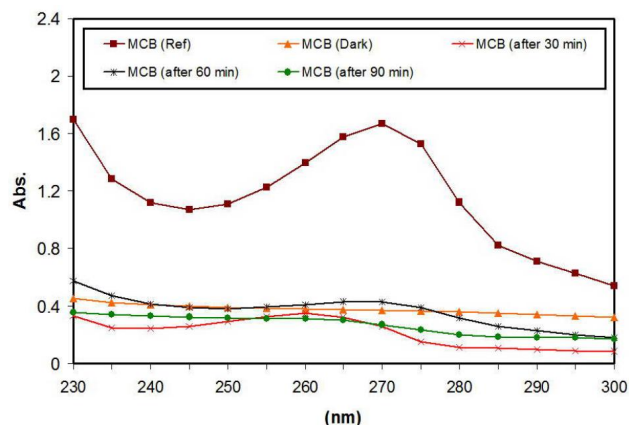


Figure 14 : Abatement performance of TiO₂/SiO₂ catalyst on MCB degradation under UV light

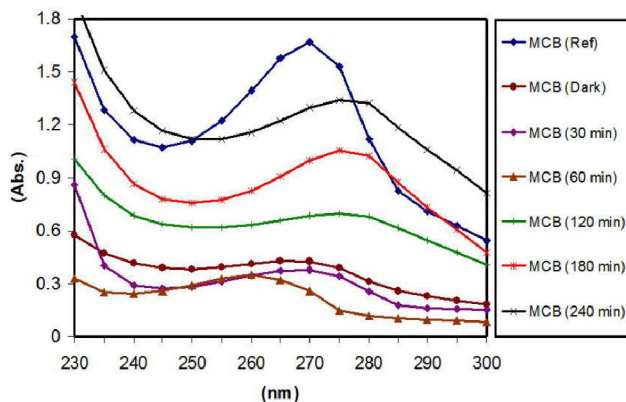


Figure 15 : Abatement performance of TiO₂/SiO₂ catalyst on MCB degradation under visible light

CONCLUSION

Synthesis of titania/silica mixed oxides is needed to

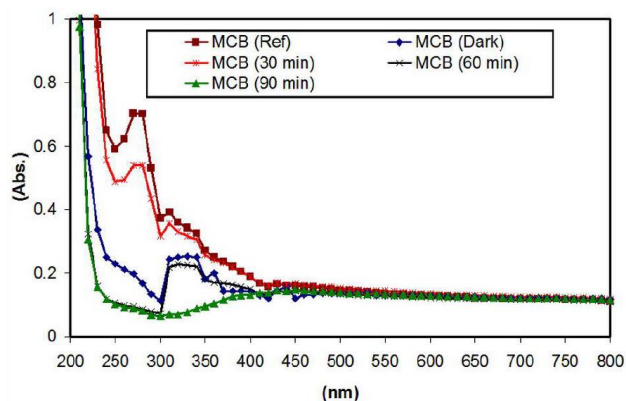


Figure 16 : Abatement performance of Pt-TiO₂/SiO₂ type (B) catalyst on MCB degradation under visible light

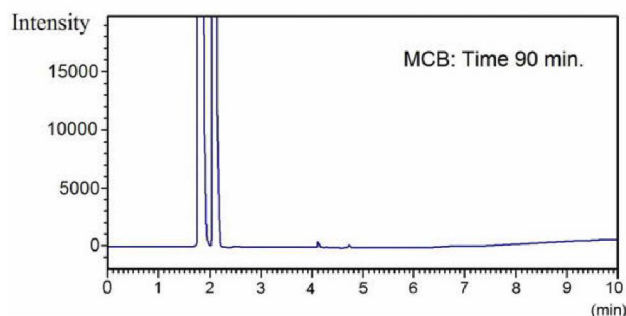
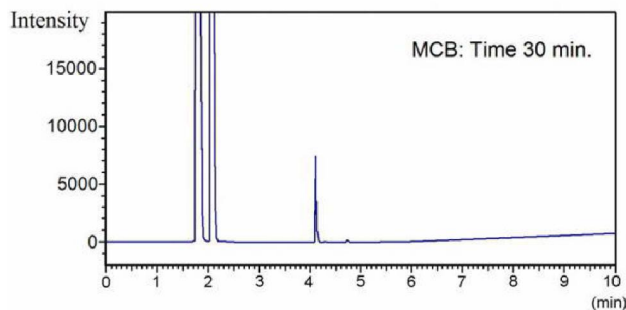
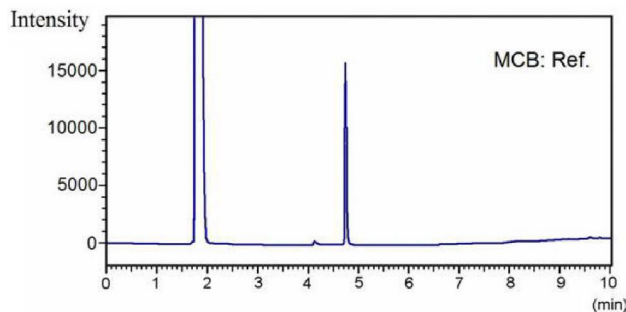


Figure 17 : The GC analysis of MCB degradation by Pt-TiO₂/SiO₂ type (B) under visible light in different times (0, 30 & 90 min)

overcome present drawbacks of pure titanium powder as regards its application. High activity of TiO₂/SiO₂ photocatalyst can be mainly attributed to the combination of surface area increment and connection bands

between titanium species and SiO₂ matrix. In order to improve the photocatalytic activity of TiO₂, particles such as SiO₂ and Pt were used. Elemental analysis of TEM images confirms the existence of Si and Pt and results showed that 0.25 grams of TiO₂/SiO₂ and Pt-TiO₂/SiO₂ type (B) at pH=3 are the best conditions for degradation of monochlorobenzene at temperature < 40°C under UV and visible light respectively. This is in marked contrast to the photocatalytic degradation of many organic compounds in the presence of TiO₂ under ultraviolet irradiation, in which intermediates are easily detected by absorption spectra^[28]. For example Almquist et. al. have reported oxidation of MCB at temperature < 300 °C using V₂O₅/TiO₂ nanostructure as a catalyst without irradiation. They founded that MCB is stable in the presence of V₂O₅/TiO₂ catalyst at temperature up to 300 °C and they observed stable organic byproducts of MCB oxidation at temperature < 400 °C. But our recent results showed that the activity of Pt-TiO₂/SiO₂ (type (B)) which is synthesized in this work has been increased considerably in comparison with V₂O₅/TiO₂ catalyst reported by Almquist et. al.

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