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PREPARATION AND PHOTOCATALYTIC ACTIVITY OF IRON-MODIFIED TITANIUM DIOXIDE PHOTOCATALYST

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Abstract. Iron modified TiO₂ was prepared by the sol-gel method and surface modification method followed by calcination at 400°C. Two types of titanium dioxide: TiO₂ ST-01 (Ishihara Sangyo Ltd., Japan; 300 m²/g), and TiO₂ P25 (Evonik, Germany, 50 m²/g) were used in the grinding procedure. The photocatalysts were characterized by UV-VIS absorption and BET surface area measurements. The photocatalytic activity of the obtained powders in UV-Vis and visible light was estimated by measuring the decomposition rate of phenol (0.21 mmol/dm³) in an aqueous solution. The best photoactivity under visible light was observed for iron doped TiO₂ with 0.5% by grinding the TiO₂ ST-01.

keywords: photocatalysis, modified TiO₂, iron nanoparticles, photocatalysis

1. Introduction

The process of photocatalysis using semiconductor suspension is a method widely used in environmental protection. One of the most commonly used photocatalysts, due to its characteristics (inexpensive, insoluble under most conditions, photochemically stable and non toxic), is titanium dioxide used, *inter alia*, for the elimination of organic substances from gas and liquid phases and recently also for reduction of CO₂ into the light hydrocarbons. Since pure TiO₂ absorbs UV almost exclusively, most of the work carried out in the world is focused on obtaining TiO₂ active under visible light. Modification of metals may increase the activity of titanium oxide(IV) in the range of visible light ($\lambda > 400$ nm), and thus allows the use of renewable energy - solar radiation in the environment (Valenzuela et al., 2009). Among various dopants, the Fe³⁺-dopant is the most frequently employed one, owing to its unique half-filled electronic configuration, which narrows the energy gap while inducing new intermediate energy levels and may also diminish the recombination of electrons and holes by capturing photogenerated carriers (Liu et al., 2011; Zhou et al., 2006). Liu et al. (2011) proposed the possible mechanism of Fe³⁺-dopant effect on photocatalytic activities. According to the energy level chart of Fe³⁺-dopants in TiO₂ proposed by

previous researches, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ energy level is just below the conduction band of TiO_2 while the $\text{Fe}^{3+}/\text{Fe}^{4+}$ energy level is slightly above the valence band of TiO_2 . The Fe^{3+} -dopant can act not only as a temporary trapping site of photo-induced electrons but also as a shallow capturing site of photo-induced holes, which will efficiently separate the photo-excited electrons and holes and prolong their lifetime. Furthermore, according to the viewpoint of crystal field theory, the Fe^{3+} -dopant is more stable in TiO_2 because of its $3d^5$ (half-filled high spin) electronic configuration, so the captured electrons or holes can be easily released from Fe^{2+} or Fe^{4+} to regenerate Fe^{3+} and then migrate to the photocatalysts' surface to initiate the photocatalytic reactions. On the other hand, Fe^{3+} -dopant effectively extends the UV-Vis spectra of TiO_2 into visible light region (Liu et al., 2011).

Synthetic iron oxide magnetite (Fe_3O_4) nanoparticles have been widely studied in the last decades, and an increasing number of scientific and technological applications have been developed, such as catalysts, pigments, gas sensors, biotechnology, and data storage solid support for enzymes, such as cellulase, glucose oxidase, bovine serum albumin homing peptides and lipase. Magnetite bounded to chitosan acts as a nano-absorbant for the removal of heavy metals, and when using a highly active heterogeneous Fenton system based on iron metal and magnetite, $\text{Fe}^0/\text{Fe}_3\text{O}_4$ has been used to oxidize synthetic dyes (Valenzuela et al., 2009; Jiao et al., 2010). Hematite nanoparticles are an interesting material for fundamental research because of their magnetic characteristic (Zboril et al., 2002). They can display three critical temperatures: Neel temperature, Morin temperature and blocking temperature (Zysler et al., 2001).

Recently, several methods have been developed to prepare Fe_2O_3 - TiO_2 composites, which usually exhibit improved properties. Liu et al. (2011) prepared the Fe-doped TiO_2 nanorod clusters and monodispersed nanoparticles by a modified hydrothermal and solvothermal method. The well-controlled microstructures and morphologies enhance specific surface areas of the Fe-doped TiO_2 photocatalysts compared with P25 and N-doped TiO_2 nanoparticles. High photocatalytic activities of the Fe-doped photocatalysts could be related to enhanced specific surface areas, visible light responses and diminish recombination rates of the photo-excited carriers (Liu et al., 2011).

Shi et al. (2011) obtained co-doped titanium dioxide (Fe-La-TiO_2) photocatalysts by a sol-gel method. Co-doping causes absorption spectra of Fe-La-TiO_2 to shift to the visible region and photocatalytic activity of Fe,La-TiO_2 is markedly improved due to the cooperative action of the two dopants, Fe and La (Shi et al., 2011). Iron(III)-doped titanium dioxide photocatalysts from aqueous titanium(III) chloride solution in the presence of dissolved FeCl_3 (0–10.0 at.% relative to TiCl_3) by the co-precipitation method were prepared by Ambrus et al. (2008). The photocatalytic efficiency of iron-doped titanias was found to be superior to the bare TiO_2 under UV-Vis irradiation. The photocatalyst with 3.0 at.% iron was the most efficient for the photocatalytic decomposition of phenol in UV-vis experiments. The optimal iron content was found



to be 1.2 at.% for VIS light irradiation. At higher iron contents (6.0– 10.0 at.%) the photocatalytic performance under Vis irradiation was worse relative to the undoped TiO_2 (Ambrus et al., 2008).

When titania suspensions are used, the photocatalyst must be recovered at the end of the treatment, either by filtration or sedimentation, which is expensive in terms of time and reagents. The aim of this study was to develop a method for obtaining TiO_2 modified with magnetic iron oxide (Fe_2O_3) nanoparticles and to characterize the obtained photocatalysts. BET surface area measurements, UV-Vis spectroscopy and photooxidation of phenol (under UV-Vis and visible light) were used to characterize and evaluate the photocatalytic activity of the obtained samples.

2. Materials and methods

ST-01 TiO_2 powder having anatase crystal structure was obtained from Ishihara Sangyo, Japan (anatase, surface area $300 \text{ m}^2/\text{g}$, particle size 7 nm) and P-25 from Evonik GmbH, Germany (anatase:rutile = 80:20, surface area $50 \text{ m}^2/\text{g}$, particle size 8 nm). Titanium(IV) isopropoxide, TIP, (97%) was obtained from Aldrich Chem. Fe_2O_3 nanoparticles (20 wt. % in ethanol, particle size < 110 nm) from Sigma-Aldrich Co. was used as iron source in the preparation procedure without further purification.

Gemini V (model 2365) was used for measurements of BET surface area of the catalysts. All the samples were degassed at 200°C prior to nitrogen adsorption measurements. BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3.

The diffuse reflectance spectra DRS were characterized using the UV–Vis spectrometer (UVD 3500 Labomed, USA) equipped with an integrating sphere accessory for diffuse reflectance.

In the sol–gel method, Fe-doped TiO_2 catalysts were prepared from titanium(IV) isopropoxide, known to be the titanium source origin for the anatase-type TiO_2 . Titanium(IV) isopropoxide ($V = 20 \text{ cm}^3$) were mixed with an appropriate amount of the dopant precursor (solution of iron oxide in ethanol) and distilled water ($V = 35 \text{ cm}^3$). The solution was being stirred at room temperature for 30 min, followed by a 24-hour thermal treatment (80°C) and calcinations at 400°C for 2 h. The procedure is presented by a simplified block diagram in Fig. 1A.

In the second procedure iron-modified TiO_2 powders were prepared by grinding 3 g of either ST-01 TiO_2 or P25 TiO_2 in an agate mortar with iron oxide in ethanol. The obtained powders were dried for 24 h at the temperature of 80°C and calcinated at 400°C for 2 h.. The procedure is presented by a simplified block diagram in Fig 1B.

The photocatalytic activity was determined by measuring the decomposition rate of phenol (0.21 mM) aqueous solution which was selected as a model contaminant under UV-Vis and visible irradiation. Photocatalytic degradation runs were preceded by blind tests in the absence of a catalyst or illumination.

Twenty five milliliters of a photocatalyst suspension (125 mg) were stirred using magnetic stirrer and aerated ($5 \text{ dm}^3/\text{h}$) prior and during the photocatalytic process.



Aliquots of 1.0 cm^3 of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters ($\text{Ø} = 0.2 \text{ mm}$) to remove photocatalyst particles. Phenol concentration was estimated by a colorimetric method using a UV–Vis spectrophotometer. The suspension was irradiated using 1000 W Xenon lamp (Oriol), which emits both UV and Vis light. To limit the irradiation wavelength, the light beam was passed through GG 420 to cut-off wavelengths shorter than 420 nm.

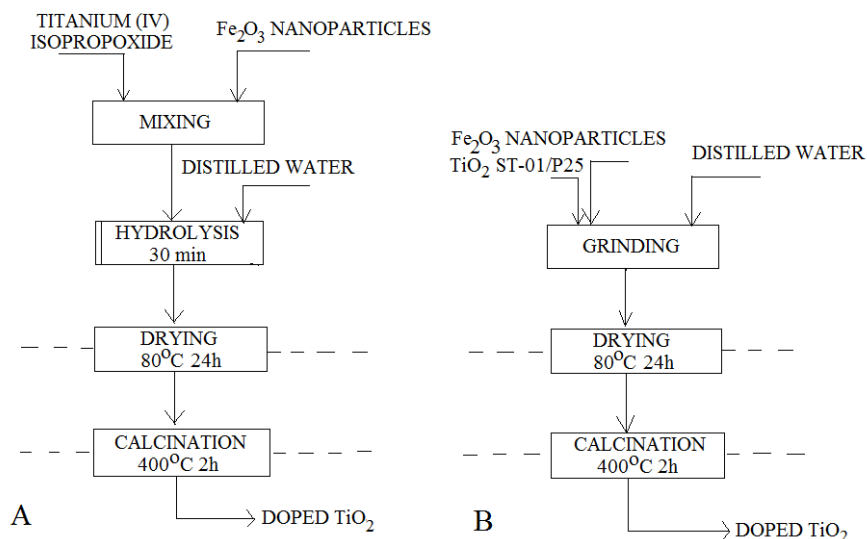


Fig. 1. Block diagram of Fe-doped TiO₂ prepared by (a) sol-gel method, (b) impregnation method

3. Result and discussion

The amount of the dopant taken for photocatalyst preparation was calculated on the assumption that the content of iron in the photocatalyst after synthesis should be equal to from 0.5 to 10 wt.% of the catalyst dry mass. Sample numbers, the amount of the dopant used during preparation, TiO₂ matrix and BET surface area are presented in Table 1. All the photocatalysts obtained in this work were in the form of orange powders.

Photocatalytic activity of the obtained TiO₂ powders was estimated by measuring the decomposition rate of phenol in aqueous solution in the presence of UV-Vis or visible light irradiation ($\lambda > 420 \text{ nm}$). No degradation of phenol was observed in the absence of either photocatalyst or illumination. Pure TiO₂ synthesized by the sol-gel method without any dopant, P25 TiO₂ and ST-01 TiO₂ were used as the reference system. Photocatalytic activity under UV-Vis or visible light is presented as phenol degradation rate (Table 1) and as efficiency of phenol removal after 60 min of irradiation (Fig. 2).



Table 1 . Surface properties and photocatalytic activity of iron-doped TiO₂ photocatalysts – the influence of dopant and preparation method

Sample label	Metal precursor	TiO ₂ matrix ^a	Content of metal precursor [wt. %]	BET [m ² /g]	Phenol degradation rate [μmol·dm ⁻³ ·min ⁻¹]	
					UV/Vis	Vis (λ>420 nm)
Fe(0,5)_H	Fe ₂ O ₃ /EtOH	TIP	0.5	180	3.04	0.33
Fe(1)_H			1	166	2.54	0.26
Fe(2)_H			2	154	1.16	0.29
Fe(3)_H			3	152	1.26	0.19
Fe(5)_H			5	152	0.72	0.57
Fe(10)_H			10	143	0.87	0.09
Fe(0,5)_ST	Fe ₂ O ₃ /EtOH	ST-01	0.5	215	3.04	2.00
Fe(1)_ST			1	149	2.01	0.76
Fe(2)_ST			2	151	1.96	0.54
Fe(3)_ST			3	140	1.15	0.85
Fe(5)_ST			5	129	1.49	0.78
Fe(10)_ST			10	129	1.48	0.22
Fe(0,5)_P25	Fe ₂ O ₃ /EtOH	P25	0.5	58	3.08	0.34
Fe(1)_P25			1	53	3.80	0.23
Fe(2)_P25			2	55	3.63	0.07
Fe(3)_P25			3	56	2.92	0.39
Fe(5)_P25			5	56	3.24	0.06
Fe(10)_P25			10	62	2.36	0.09
P25	-	-	-	50 (58 ^b)	2.90	0.18
ST-01	-	-	-	300 (278 ^b)	2.82	0.50
TiO ₂	-	-	-	161	3.07	0.16

^aTIP – TiO₂ obtained by titanium(IV) isopropoxide hydrolysis; P-25 – mixture of anatase and rutile with majority of anatase (particle size: 40 nm, S_{BET} = 50 m²/g, supplier: Evonik, Germany); ST-01 – anatase (particle size: 8 nm, S_{BET} = 300 m²/g, supplier: Ishihara Sangyo Ltd., Japan); ^b As-measured data

Doping with iron increases the photocatalytic activity under UV-Vis and visible light. Under UV-Vis light irradiation, the rate of phenol degradation in the presence of pure TiO₂ obtained by the sol-gel method, TiO₂ST01 and TiO₂ P25 was estimated to be 3.07, 2.92 and 2.82 μmol·dm⁻³·min⁻¹, respectively. The most active were the photocatalysts prepared by grinding TiO₂ P25 with a dopant. The observed rate was increased to 3.80 μmol·dm⁻³·min⁻¹ in the presence of Fe(1)_P25 doped with 1% wt. of iron. Iron modified TiO₂ST-01 and sol-gel TiO₂ showed slightly enhanced photocatalytic activities under UV-Vis irradiation as compared to pure TiO₂ST01 and sol-gel TiO₂. The highest phenol degradation rate was 3.04 μmol dm⁻³ min⁻¹ for the sample with 0.5% wt. of iron - Fe(0,5)_ST and Fe(0,5)_H prepared by grinding TiO₂ST01 and by the sol-gel method.



Photocatalysts prepared by surface impregnation of TiO₂ ST-01 showed the highest activity in the phenol degradation reaction under visible light than those used with other arrays of TiO₂.

Under visible light irradiation, the rate of phenol degradation in the presence of pure TiO₂ obtained by the sol-gel method, TiO₂ ST01 and TiO₂ P25 was estimated to be 0.52, 0.50 and 0.12 $\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$, respectively. The best photoactivity under visible light was observed for the sample prepared by grinding TiO₂ ST-01 with 0.5% wt. of iron. In the presence of the Fe(0.5)_ST sample, phenol was degraded in 61% after 60 min. of irradiation. Using the TiO₂P25 matrix, we could notice the lack of photocatalytic activity under visible light.

Figure 2 shows a comparison of characteristics of the most photoactive samples prepared using three types of TiO₂ matrix under UV-Vis (Fig. 2A) and visible (Fig. 2B) light. All the photocatalysts revealed the highest photoactivity under UV-Vis and visible light comparable to that of pure TiO₂.

The amount of the dopant also influenced the specific surface area BET of the obtained photocatalysts (Table 1). The specific surface area of pure TiO₂, obtained by TIP hydrolysis, TiO₂ ST-01 and TiO₂ P25 was 161, 278 and 58 m²/g, respectively. The value of BET surface area generally decreases with increasing of iron concentration (Table 1). For all the samples prepared by the surface impregnation method the BET surface area was lower than that for pure TiO₂ST-01 and ranged from 129 to 215 m²/g. Not too much difference in the surface area was observed for the samples obtained by surface impregnation of TiO₂ P25 (the surface area varied from 53 to 62 m²/g). For the samples obtained by the sol-gel method, the surface area decreased from 180 to 143 m²/g since the amount of iron precursor added during the preparation increased from 0.5 to 10 wt.%.

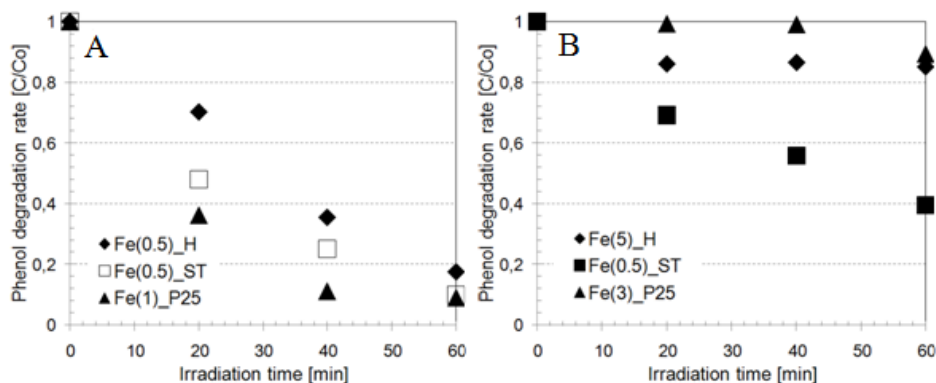


Fig. 2. Photoactivity under (A) UV-Vis and (B) Vis light of Fe-TiO₂ photocatalysts. Experimental conditions: $C_o=0.21$ mM; m (TiO₂) = 125 mg, $T=10^\circ\text{C}$, $Q_{\text{air}}=5$ dm³/h

The visible light absorbance is an important ability for photocatalysts, since solar light usage is a widely concerned issue in the practical application of photocatalysts. Absorption properties of iron-doped TiO₂ were estimated by UV-Vis spectroscopy to characterize the light absorption ability of the prepared photocatalysts. For



comparison, the spectrum of pure TiO_2 is also shown. The spectrum of bare TiO_2 clearly shows an absorption onset at about 395 nm which is in good agreement with the band gap value of bulk anatase ($\lambda = 387$ nm corresponding to 3.2 eV).

Figure 3 shows the absorption spectra of Fe- TiO_2 . The measurement of the samples was made at the wavelength of light in the range from 300 to 600 nm. When the value was of 350 to 400 nm, we observed a sharp increase in absorbance. Experimental data clearly indicate a correlation between absorption and the amount of a dopant. The higher the concentration of iron the stronger absorption in the visible range. Photocatalysts prepared by surface impregnation of TiO_2 P25 were inactive in the reaction of phenol degradation under visible light, but they revealed stronger absorption in the visible region than pure TiO_2 P25.

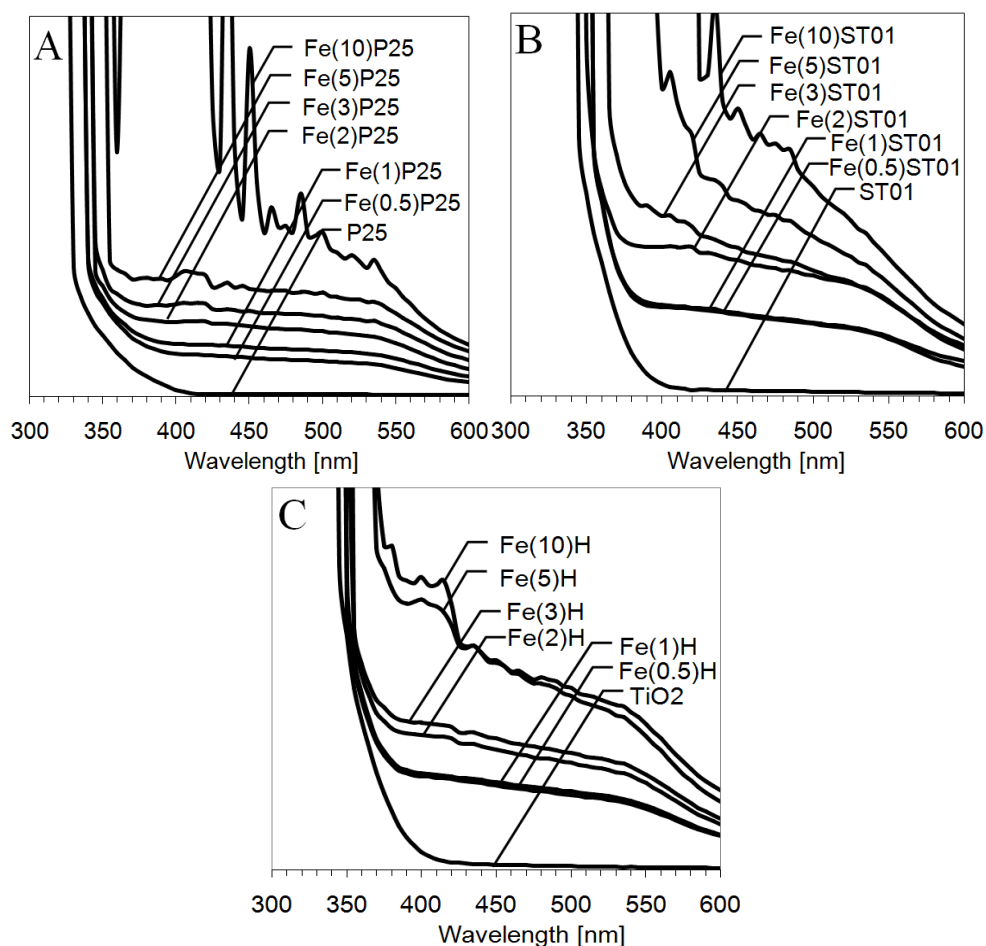


Fig. 3. Diffuse reflectance spectra of pure and Fe-modified TiO_2 prepared by (A) grinding TiO_2 P25 with a dopant (B) grinding TiO_2 ST-01 with a dopant (C) sol-gel method

4. Conclusion

Fe-modified TiO₂ nanopowders were prepared by the sol-gel and impregnation method. The amount of Fe(III) ions incorporated into TiO₂ significantly affected the characteristics and activity of the photocatalysts. The co-doped TiO₂ powders possessed a specific surface area in the range of 53-215 m²/g. The photocatalytic activity of TiO₂ was enhanced under UV-Vis light and the absorption range was extended towards the visible region. A photocatalytic degradation process was developed using phenol as a model compound.

Photocatalysts prepared by grinding TiO₂ ST-01 with a dopant were active in the reaction of phenol degradation ($\lambda > 420$ nm). The sample Fe(0.5)_ST containing 0.5 wt%. iron, calcined at 400°C (1h), showed the highest activity. After 60 min of irradiation under visible light 61% of phenol was degraded. Photocatalysts prepared by sol-gel and impregnation of TiO₂ P25 are nonactive in the reaction of phenol degradation under visible light.

All Fe-TiO₂ nanopowders were active under UV-Vis light. Sample Fe(1)_P25 showed the highest activity. After 60 min of irradiation under UV-Vis light 91% of phenol was degraded.

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