Photocatalytic Degradation of β-carotene with TiO₂ and Transition Metal Ions Doped TiO₂ under Visible Light Irradiation

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Abstract  β-carotene, one of the carotenoids, was photodegraded under visible light irradiation by using pure TiO₂ and M-TiO₂ (M= metal; Ag, Fe, Ru). The photocatalysts were prepared by a sol-gel method and incipient wetness impregnation method, and investigated by means of X-ray diffraction and scanning electron microscopy for characterization. The effects of photocatalyst and oxygen content were investigated, which was based on the absorbance at 450 nm of photodegradation of β-carotene as the main index. The study of photocatalytic activity indicated that Ag-doped TiO₂ showed higher photocatalytic activity than other photocatalysts. And also a quick decrease of β-carotene in the presence of oxygen was observed. β-cyclocitral, 5,6-epoxy-β-ionone and dihydroactinidiolide, the main photocatalytic degradation products of β-carotene were confirmed by gas chromatograph-mass spectrometer (GC-MS) analysis. All these degradation products can be used for fragrance and flavoring agents, such as cigarette flavoring ingredients.

Keywords  β-carotene, M-TiO₂, Photocatalytic Degradation, Sol-gel Method, GC-MS Analysis, Cigarette Flavoring

1. Introduction

Carotenoids are organic pigments which contain two classes, Xanthophylls and carotene. The main difference between them is whether they contain oxygen or not. All carotenoid are tetraterpenoids, which are formed with 8 isoprene molecules and contain 40 carbon atoms[1]. β-carotene, one of the carotenoids, and its degradation products are often found in tobacco, fruit and plant[2-4], which can be synthesized from vitamin A[5], also it can be cut via the cross metathesis to retinoids[6]. β-carotene is sensitive to light, temperature and oxygen, and its degradation products have been mentioned by many former researches. Many authors have mentioned about the thermal degradation of β-carotene in aqueous or oil system[7-9]. Kanasawud and his colleague studied the mechanism of how degradation products formed by heat treatment[10]. Isoe early reported that the degradation of β-carotene in aqueous system depended on oxygen and illumination intensity, and the photo oxygenation products mainly contained dihydroactinidiolide (DHA) [11]. These are very useful spices. Robert Aman and his colleagues reported the effect on the degradation and isomerization between the lutein and β-carotene under thermal treatment and light exposure , and also they made a comparison of stabilities between pure carotenoids and chloroplast-bound carotenoids for the first time[12].

Taking the environmental protection and energy into consideration, light is a kind of clean energy[13]. In order to use the visible light for the photodegradation of β-carotene, it is important to screen the photocatalyst. In many fields, TiO₂ has been used as photocatalyst because of its stability, cleanness and catalysis efficiency. It has been extensively studied in the degradation of organic pollutants under UV irradiation ( <387nm ). While one obstacle of this material is the band gap, only 5% (UV light) can be absorbed by TiO₂, so the improvement of the photocatalytic efficiency of TiO₂ is to shift its optical response from UV range to the visible range[14]. For this purpose, in the last decades, the metal ions doped TiO₂ has been widely studied. Many organic substances can be degraded by using the Fe-TiO₂ catalysts, like 2,4-dichlorophenol[15], maleic acid[16] and gas-phase ethanol[17]. In the meantime, the effect of photocatalytic activity of TiO₂ can be also efficiently improved by the dopant of silver[18,19]. Due to the fact that textile industries produce a large amount of dye pollutants, most of them are azo dyes which contain conjugated double bond[20], Ag-TiO₂ can be used in photocatalytic degradation of them,
like Direct Red 23[21], Crystal Violet, Methyl Red dye[22-24], etc. To our knowledge, the photocatalytic degradation of β-carotene over transition metal doped TiO2 under visible light irradiation has been hardly reported.

The purpose of our work was to study the photodegradation of β-carotene over transition metal (Ag+, Fe3+, Ru2+) doped TiO2 under visible light irradiation and obtain the flavor substances employed as the cigarette flavoring ingredients. In this paper, the transition metal doped TiO2 selected as catalysts were prepared by sol-gel method and incipient wetness impregnation method. While compared with pure TiO2 and P25, the results indicated that the Ag-doped TiO2 demonstrated high photocatalytic activity in the system of β-carotene degradation.

2. Experimental

2.1. Photocatalysts Preparation

2.1.1. Sol-gel Method

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The synthesis was done by the hydrolysis of titanium (IV) tetrabutoxide (TNTB) as a precursor in mixed solution of glacial acetic acid and anhydrous ethanol. 17.0 mL TNTB and 4.8 mL glacial acetic acid were dissolved in 34 mL anhydrous ethanol, and stirred for 30 min. 1 mL distilled water and 10 mL anhydrous ethanol were added dropwise to let the hydrolysis process take place. After an hour, the pale yellow, stable, well-distributed, transparent TiO2 gel was obtained, and aged for 2 days. The TiO2 gel was dried at 373 K for 32 h and then ground. The dried powder was calcined at 773 K for 2 h to obtain pure sol-gel TiO2 powder in muffle furnace.

TiO2 doped with Ag, Fe and Ru series catalysts were synthesized by sol-gel method. Transition metal ions were doped into TiO2 with the doping content of 4 mol% by adding AgNO3, FeCl3 and Ru(bpy)3Cl2·6H2O in the distilled water prior to hydrolysis of TNTB, respectively.

2.1.2. Incipient Wetness Impregnation Method

1 g Nano TiO2 (P25 anatase) was dispersed in 25 mL distilled water. Doping was performed by impregnation of TiO2 with aqueous solution of AgNO3, FeCl3 at room temperature. The mixture was stirred for 12 h. Then, water was evaporated by heating at 343 K. At last, the photo catalysts were calcined at 773 K for 4 h. Metallic solution concentration was the one required to obtain 4 mol% of doping content [25].

2.2. Equipment

X-ray diffraction (XRD) analysis of M- TiO2 series samples were performed via using a diffractometer (Bruker D8) with CuKα irradiation (λ = 1.541 Å), of which 2θ range was 10-70°. The size and surface morphology of TiO2 particles were observed by Scanning Electron Microscope (SEM, Hitachi S-4800). 23 W white fluorescent lamp (Philips Tornado 23 W E27) was used as the visible source. The UV-Vis spectrophotometer (Agilent 8453) was used to obtain the absorption spectrum of β-carotene, and followed the track of the degradation. Gas Chromatography –Mass Spectrometer (Agilent 6890GC/ 5973N) was carried out to the separation and analysis of β-carotene. The degradation products were separated by using DB-5MS (30 m × 0.25 mm × 0.25 μm) column (Agilent). The pressure of carrier gas, helium gas, was 10 psi. The temperature of injection port was 533 K and the carrier gas flow was 1mL min⁻¹; the Gas Chromatography operated at 323 K, then programmed to 473 K at 5 K min⁻¹, and held 4 min; then programmed to 533 K at 25 K min⁻¹, and held 4 min. The sample volume was 1 μL, the split ratio was 10:1 and the solvent delay was 5 min. The source temperature was 423 K and the ionization energy was 70 eV. The degradation products were identified by automatic search in Nist98 library and quantified by peak area normalization method.

2.3. Experimental Conditions

10 mg β-carotene and 0.15 g Nano TiO2 was suspended by sonication in 50 mL of solvents in 150 mL light reaction tube for 10 min to make the β-carotene completely dissolved in solvent. Then under the condition of a certain temperature (298 K), the photocatalytic degradation started by magnetic stirring under visible light irradiation until the β-carotene suspension turned into a transparent solution. (In some experiments, the suspensions were saturated with nitrogen or with oxygen before sealing the light reaction tube.) After the reaction completed, the suspensions were centrifuged for 10 min to get supernatant fluid. The liquid were filtered for GC-MS detection, and then the analysis results of degraded product composition were obtained.

3. Results and Discussion

3.1. Characterization of Morphology and Structure of TiO2 Particle

Figure 1 show that by using the sol-gel method, metal ions doped catalysts were compared to pure TiO2 (calcined at 773 K). At 773 K, As to Ag doped TiO2, the analysis of XRD showed mainly anatase phases, while TiO2 with 4mol% Fe were the mixture of rutile and anatase phases. Because of the low concentration, Ru2+, Ag+ and Fe3+ were not high enough to allow its detection in the catalysts.

Also XRD analysis had been obtained from the P25 and P25 with 4mol% doped M (Ag, Fe) (Fig. 2). However, the presence of iron or silver was also not detected.
Photocatalytic Degradation of β-carotene with TiO$_2$ and Transition Metal Ions Doped TiO$_2$ under Visible Light Irradiation

Figure 1. XRD patterns of the TiO$_2$ powders by using the sol-gel method (calcined at 773 K) (A) pure TiO$_2$ and 4 mol% metal ions doped TiO$_2$ (B) Ru-doped TiO$_2$, (C) Ag-doped TiO$_2$, (D) Fe-doped TiO$_2$.

Figure 2. XRD patterns of the TiO$_2$ powders by using the wetness impregnation method (calcined at 773 K) 4 mol% metal ions doped P25 (E) Fe-doped P25, (F) Ag-doped P25 and (G) P25.
The crystallite sizes of pure TiO$_2$ and doped TiO$_2$ were estimated from the peak FWHM (full width half maximum) by using the Scherrer equation and shown in Table 1.

Table 1. Physical properties of 4mol% M-TiO$_2$ series samples, pure TiO$_2$ and P25

| Samples   | Phase    | Crystallite size /nm |
|-----------|----------|-----------------------|
| TiO$_2$   | anatase  | 16.7                  |
| 4mol% Ru-TiO$_2$ | rutile   | 106.6                 |
| 4mol% Ag-TiO$_2$ | anatase  | 11.6                  |
| 4mol% Fe-TiO$_2$ | anatase, rutile | 44.7                |
| 4mol% Fe-P25 | anatase  | 36.0                  |
| 4mol% Ag-P25 | anatase  | 24.1                  |
| P25       | anatase  | 28.8                  |

It was found that the crystallite size was in the range of 11.6-44.7 nm, except Ru-TiO$_2$. The sizes were 16.7, 106.6, 11.6, 44.7, 36.0, 24.1, 28.8 nm, respectively. Among them, the size of Ru-TiO$_2$ was larger than average. It indicated that the same dopant of Ru led to the increase of the crystallite size. Meanwhile, the phase of Ru-TiO$_2$ was mainly rutile. Statistics indicated that the dopant of Ag promoted the decrease of crystallite size, while the dopant of Fe promoted a little bit increasing of the size.

Figure 3 shows the SEM image of surface morphology of TiO$_2$ and metal-doped particles through hydrolytic process and calcination at 773 K. From SEM images, the nanoparticles sizes were approximately 50 nm, except Ru-doped TiO$_2$ particles.

Figure 3. Observation of surface morphology of TiO$_2$ particles by SEM (calcined at 773 K) (A) pure TiO$_2$ powder; (B) Ru-doped TiO$_2$; (C) Ag-doped TiO$_2$; (D) Fe-doped TiO$_2$; (E) Fe-doped P25; (F) Ag-doped P25
3.2. Standard Curve of β-carotene in Hexane

5 mg β-carotene were dissolved in hexane, and then diluted with hexane to 100 mL in the volumetric flask, so the 50 mg/L standard solution was got. Then a set of 5 concentrations of β-carotene (1, 2, 3, 4, 5 mg/L) in 100 mL volumetric flask was obtained. By measuring the absorbance of standard solution in the wavelength of 450 nm, and the linear regressive equation was established: \( Y = 0.04177 + 0.06801 \times X \), \( R^2 = 0.99571 \).

![Figure 4. Standard curve of β-carotene in hexane](image)

3.3. Photocatalytic Activity

Figure 5 shows the decrease of concentration of β-carotene in the air under visible light irradiation (wavelengths > 400 nm). 0.25 mL reaction liquid was diluted to 10 mL, and then UV-Vis Spectrophotometer was used to follow the track of the reaction. No obvious changes of concentration of β-carotene with Fe-doped TiO2 and Fe-doped P25 were found in 300 min. The Ag-doped TiO2 and Ag-doped P25 show a higher photocatalytic activity than other photocatalysts. Meanwhile, Ag-doped TiO2 was a little better than Ag-doped P25, as it achieved a decrease of approximately 76% of the concentration of β-carotene. In the presence of P25 and pure TiO2, the concentration of β-carotene decreased 30% and 28% in 300 min. However, Ru-doped TiO2 showed very lower photocatalytic activity in 300 min.

The degradation of β-carotene in the presence of air, oxygen and nitrogen was followed at room temperature with Ag-doped TiO2 under visible light irradiation. The method of dilution was same as above. Obviously, in the presence of nitrogen atmosphere, there was almost no change of concentration. It indicated that photodegradation of β-carotene in the nitrogen atmosphere was very slow. Shown in Figure 6 is observed a quick decrease of β-carotene in the oxygen atmosphere. With achieving a decrease of approximately 86% of the concentration, it has the highest level in the photocatalytic degradation of β-carotene.

![Figure 5. Comparison of the photocatalytic degradation of β-carotene in the presence of pure TiO2, Ru-doped TiO2, Ag-doped TiO2, Fe-doped TiO2, Fe-doped P25, Ag-doped P25 and P25 powders under visible light irradiation.](image)

![Figure 6. Comparison of the photocatalytic degradation of β-carotene in the presence of oxygen, air and nitrogen with Ag-doped TiO2](image)

3.4. Identification of Compounds

Figure 7 shows the gas chromatograms of the photocatalytic degradation products from β-carotene. Since the photodegradation experiment was carried out at room temperature (298 K), eight of the compounds were identified. The structures and retention time were shown below.
The compounds isolated under visible light are given in Table 2. Most of them have been identified in the other system before, like the thermal degradation of β-carotene in the solution [10]. The major photocatalytic degradation products contain esters, ketones, alcohols and aldehydes. Among these degradation products, 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone), 2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde (β-cyclocitral), β-ionone, 5,6-epoxy-β-ionone and dihydroactinidiolide are all spice materials. In the detection of the components, isophorone has an aroma of mint or camphor, which can increase the flavor of cigarette. β-cyclocitral is fruity. β-ionone, which is the main source of rose fragrance, and is also an important spice. Adding β-ionone into the tobacco can increase the unique aroma of the cigarette. Dihydroactinidiolide’s addition can also achieve the same effect.

**Table 2.** Photocatalytic degradation products of β-carotene in the presence of oxygen at room temperature

| Peak (FIG.8.) | Degradation products | Retention time | Chemical formula | Molecular formula | Molecular weight |
|---------------|----------------------|----------------|------------------|-------------------|-----------------|
| 1             | 2-methyl-2-hepten-4-one | 7.382          | C<sub>8</sub>H<sub>14</sub>O | C<sub>8</sub>H<sub>14</sub>O | 126             |
| 2             | 2,2,6-trimethylcyclohexanone | 8.358         | C<sub>9</sub>H<sub>16</sub>O | C<sub>9</sub>H<sub>16</sub>O | 140             |
| 3             | 3,5,5-trimethyl-2-cyclohexen-1-one | 9.001      | C<sub>9</sub>H<sub>14</sub>O | C<sub>9</sub>H<sub>14</sub>O | 138             |
| 4             | 2,6-dimethylcyclohexanol | 10.409        | C<sub>10</sub>H<sub>16</sub>O | C<sub>10</sub>H<sub>16</sub>O | 128             |
| 5             | 2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde | 13.468   | C<sub>10</sub>H<sub>16</sub>O | C<sub>10</sub>H<sub>16</sub>O | 152             |
| 6             | β-ionone              | 20.286        | C<sub>13</sub>H<sub>20</sub>O | C<sub>13</sub>H<sub>20</sub>O | 192             |
| 7             | 5,6-epoxy-β-ionone    | 20.375        | C<sub>13</sub>H<sub>18</sub>O<sub>2</sub> | C<sub>13</sub>H<sub>18</sub>O<sub>2</sub> | 208             |
| 8             | dihydroactinidiolide  | 21.497        | C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> | C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> | 180             |
3.5. The GC-MS Analysis of the Photocatalytic Degradation Products

According to the compositional analysis of degradation products, and comparison of the content of degradation products percentage, β-cyclocitral, 5,6-epoxy-β-ionone and dihydroactinidiolide were the major products and selected to carry out a comparative analysis. These three kinds of substances were also the important sources of aroma.

Figure 8 shows that in the different gas atmosphere, oxygen, air, nitrogen, respectively, with other conditions unchanged (room temperature, Ag-doped TiO$_2$ as photocatalyst), oxygen content was changed to analyze how it influenced the degradation products of β-carotene. In the presence of pure oxygen, more dihydroactinidiolide was obtained. While 5,6-epoxy-β-ionone was obtained more than other two situations in the air atmosphere, correspondingly, the content of DHA was less. In nitrogenous atmosphere, not only was the degradation of β-carotene slow, but also it was not easy to generate 5,6-epoxy-β-ionone, the content was very low, but the β-cyclocitral was higher.

![Figure 8](image)

**Figure 8.** The influence of oxygen content on the degradation products of β-carotene

Figure 9 show that different photocatalysts influence the degradation products of β-carotene (in the presence of air). When Ru-doped TiO$_2$ was a photocatalyst in the degradation reaction, DHA were obtained more than others, while β-cyclocitral was hard to be detected. Meanwhile, the participant of Ru-doped TiO$_2$ degraded β-carotene very slowly, so for this degradation, maybe Ru-doped TiO$_2$ was not a good photocatalyst. Compared with other photocatalysts, 5, 6-epoxy-β-ionone was obtained more when the pure TiO$_2$ took part in the degradation.

![Figure 9](image)

**Figure 9.** The influence of different photocatalysts on the degradation products of β-carotene

4. Conclusions

Photocatalytic activity studies on β-carotene degradation with pure TiO$_2$ and metal ions doped TiO$_2$ had shown that Ag-TiO$_2$ showed a better catalytic ability than others, and in the presence of oxygen atmosphere, a quick decrease of β-carotene was observed.

From the analysis of GC-MS, eight important degradation products were identified. In the oxygen atmosphere, it was easy to produce DHA, while the content of 5, 6-epoxy-β-ionone was very low in the presence of nitrogen. When Ag-doped TiO$_2$ was a photocatalyst in this degradation reaction, it was easy to form β-cyclocitral. While compared with other photocatalysts, 5, 6-epoxy-β-ionone was obtained more when the pure TiO$_2$ took part in the degradation.

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REFERENCES

[1] E. Rodríguez-Bustamante, S. Sánchez. Microbial Production of C13-Norisoprenoids and Other Aroma Compounds via Carotenoid Cleavage. *Crit. Rev. Microbiol.* 2007, 33(3), 211-230

[2] N. J. Eggers, K. Bohna, B. Dooley. Determination of vitispirane in wines by stable isotope dilution assay. *Am. J. Enol. Vitic.* 2006, 57(2), 226-232.

[3] Y. Kotseridis, R. L. Baumes, A. Bertrand, G. K. Skourounmounis. Quantitative determination of β-ionone in red wines and grapes of bordeaux using a stable isotope dilution assay. *J. Chromatogr. A.* 1999, 848(1-2), 317-325.

[4] M. A. Sefton, G. K. Skourounmounis, R. A. Massy-Westropp, P. J. Williams. Norisoprenoids in *Vitis vinifera* white wine grapes and the identification of a precursor of damascenone in these fruits. *Aust. J. Chem.* 1989, 42(12), 2071-2084.

[5] H. J. Bestmann, O. Kratzer. Insight into β-carotene from vitamin A. *Angew. Chem.* 1961, 73(23), 757.

[6] A. Wojtkielewicz, J. Maj, J. W. Morzycki. Cross metathesis of β-carotene with electron-deficient dienes. A direct route to retinoids. *Tetrahedron Lett.* 2009, 50(33), 4734-4737

[7] D. F. Steenson, D. B. Min. Effects of β-Carotene and Lycopene Thermal Degradation Products on the Oxidative Stability of Soybean Oils. *J. Am. Oil Chem. Soc.* 2000, 77(11), 1153-1160.

[8] N. A. H. Bestmann, O. Kratzer. Synthesis of β-carotene from vitamin A. *Angew. Chem.* 1961, 73(23), 757.

[9] A. Zeb, M. Murkovic. Determination of thermal oxidation and oxidation products of β-carotene in corn oil triacylglycerols. *Food. Res. Int.* 2013, 50(2), 534-544.

[10] P. Kanasawud, J. C. Crouzet. Mechanism of formation of volatile compounds by thermal degradation of carotenoids in aqueous medium. I. β-Carotene degradation. *J. Agric. Food. Chem.* 1990, 38(1), 237-243.

[11] S. Ise, S. B. Hyeon, T. Sakan. Photo-oxidation of carotenoids. I. the formation of dihydroactinidiolide and β-ionone from β-carotene. *Tetrahedron Lett.* 1969, 10(4), 279-281.

[12] R. Aman, A. Schieber, R. Carle. Effects of Heating and Illumination on Trans-Cis Isomerization and Degradation of β-Carotene and Lutein in Isolated Spinach Chloroplasts. *J. Agric. Food. Chem.* 2005, 50(24), 9512-9518.

[13] V. I. Shapovalov. Nanopowders and films of titanium oxide for photocatalysis: A review. *Glass Phys. Chem.* 2010, 36(2), 121-157.

[14] X. T. Hong, Z. P. Wang, W. M. Cai, F. Lu, J. Zhang, Y. Z. Yang, N. Ma, Y. J. Liu. Visible- Light- Activated Nanoparticle Photocatalyst of Iodine- Doped Titanium Dioxide. *Chem. Mater.* 2005, 17(6), 1548-1552

[15] Y. M. Wu, J. L. Zhang, L. Xiao, F. Chen. Preparation and characterization of TiO₂ photocatalysts by Fe²⁺ doping together with Au deposition for the degradation of organic pollutants. *Appl. Catal. B: Environ.* 2009, 88(3-4), 525-532.

[16] J. Araña, O. González-Díaz, M. Miranda Saracho, J. M. Doña-Rodríguez, J. A. Herrera Melián, J. Pérez Peña. Maleic acid photocatalytic degradation using Fe- TiO₂ catalysts. Dependence of the degradation mechanism on the Fe catalysts content. *Appl. Catal. B: Environ.* 2002, 36(2), 113-124

[17] J. Araña, O. González-Díaz, J. M. Doña-Rodríguez, E. Tello Rendón, J. A. Herrera Melián, G. Colón, J. A. Navío, J. Pérez Peña. Gas- phase ethanol photocatalytic degradation study with TiO₂ doped with Fe, Pd and Cu. *J. Mol. Catal. A: Chem.* 2004, 215(1-2), 153-160.

[18] C. He, Y. Yu, X. F. Hu, A. Larbot. Influence of silver doping on the photocatalytic activity of titanias films. *Appl. Surf. Sci.* 2002, 200(1-4), 239-247

[19] C. He, Y. Yu, X. F. Hu, A. Larbot. Effect of silver doping on the phase transformation and grain growth of sol- gel titania powder. *J. Eur. Ceram. Soc.* 2003, 23(9), 1457-1464.

[20] V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. H. Habibi, A. Rostami-Vartoomi. Photocatalytic degradation of azo dyes catalyzed by Ag doped TiO₂ photocatalyst. *J. Iran. Chem. Soc.* 2009, 6(3), 578-587.

[21] N. Sobana, K. Selvam, M. Swaminathan. Optimization of photocatalytic degradation conditions of Direct Red 23 using nano- Ag doped TiO₂. *Sep. Purif. Technol.* 2008, 62(3), 648-653.

[22] C. Sahoo, A. K. Gupta, A. Pal. Photocatalytic degradation of Crystal Violet (C.I. Basic Violet 3) on silver ion doped TiO₂. *Dyes Pigments,* 2005, 66(3),189-196.

[23] C. Sahoo, A. K. Gupta, A. Pal. Photocatalytic degradation of methyl red dye in aqueous solutions under UV irradiation using Ag⁺ doped TiO₂. *Desalination,* 2005, 181(1-3), 91-100.

[24] A. K. Gupta, A. Pal, C. Sahoo. Photocatalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using Ag⁺ doped TiO₂. *Dyes Pigments,* 2006, 69(3), 224-232.

[25] R. I. Bickley, J. S. Lees, R. J. D. Tilley, L. Palmisano, M. Schiavetto. Characterization of iron /titanium oxide photocatalysts. 1. Structural and magnetic studies. *J. Chem. Soc. Faraday Trans.* 1992, 88(3), 377-383.