

Preparation of aluminum foil-supported nano-sized ZnO thin films and its photocatalytic degradation to phenol under visible light irradiation

Feng Peng^{*}, Hongjuan Wang, Hao Yu, Shuihui Chen

Department of Chemical Engineering, South China University of Technology, GuangZhou 510640, China

Received 6 October 2005; received in revised form 24 March 2006; accepted 29 March 2006

Available online 21 April 2006

Abstract

The zinc oxide thin films on aluminum foil have been successfully prepared by sol–gel method with methyl glycol as solvent. The film was characterized by means of XRD, TG, UV–vis, SEM and AFM, which show that the ZnO/Al film is formed by a layer of ZnO nano-sized particles with average diameter of 52.2 nm. Under the initial concentration of 20 mg/L phenol solution (500 mL) and visible light irradiation time of 3 h, more than 40% of the initial phenol was totally mineralized using two pieces of ZnO/Al thin film as photocatalyst with an efficient irradiation area of 400 cm². It is a promising visible light responded photocatalyst for the activation of O₂ at room temperature to degrade organic pollutants.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Nanostructures; A. Thin films; B. Sol–gel chemistry; D. Catalytic properties

1. Introduction

The removal of organic pollutants in wastewater is an important method in environmental protection. Many methods, including biosorption [1], conventional activated sludge treatment process [2], electrochemical technologies [3,4] and reverse osmosis [5] have been applied on wastewater treatment. Photocatalysis has been given universal attention in environment treatment and energy development fields since the discovery of photo electrochemical splitting of water on titanium dioxide (TiO₂) electrodes [6]. Most investigations have been carried out under ultraviolet (UV) light, because TiO₂ photocatalysts show relatively high activity and chemical stability under UV light [7,8], which exceed the band gap energy of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively. However, since UV light accounts for only a small fraction (5%) of the sun's energy compared to visible light (45%), the technological use of TiO₂ is largely impaired [9,10]. In recent years elimination of organic pollutants in water by oxidation through molecular oxygen and sunlight is the most environmentally friendly pollution-treatment method [11,12]. For this purpose, the development of photocatalysts with a high activity under visible light irradiation is required in order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reactions, and also is very interesting and profound to find promising photocatalysts for highly efficient utilization of visible light.

^{*} Corresponding author. Tel.: +86 20 88375816; fax: +86 20 87113735.

E-mail address: cefpeng@scut.edu.cn (F. Peng).

As a well-known photocatalyst, ZnO has been paid much attention in the degradation and complete mineralization of environmental pollutants [13]. Since ZnO has approximately same band gap energy (3.2 eV) as TiO₂, its photocatalytic capacity is anticipated to be similar to that of TiO₂. Further studies have confirmed that ZnO exhibits more efficiency than TiO₂ in visible light photocatalytic degradation of some dyes, even in aqueous solution [14,15].

On the other hand, the use of conventional powder catalyst results in disadvantages in stirring during the reaction and in the separation of powder after the reaction. Preparation of film catalysts will make it possible to overcome these disadvantages and to extend the industrial applications [16]. The sol–gel process, as a simple and easy dip-coating means, is one of the versatile methods to prepare thin film-supported nano-sized particles without complicated instruments such as CVD. Thin film photocatalysts with their high photocatalytic ability, high stability, convenient reuse, have received more and more attention. However, there has been little success in finding thin film photocatalyst that can operate effectively with visible light as yet. In this paper, a commercial aluminum foil was successfully used as substrate to prepare nano-sized ZnO film. The ZnO/Al films have been employed in photocatalytic degradation of wastewater with phenol. The result shows that the film is a new visible-driven photocatalyst with higher activity. It is very interesting and significant to research promising photocatalysts for high efficient utilization of solar energy.

2. Experimental

2.1. Preparation of aluminum foil-supported ZnO thin films

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, denoted as ZAD), methyl glycol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), monoethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$, denoted as MEA), aluminum foil (0.1 mm × 100 mm × 200 mm) and phenol ($\text{C}_6\text{H}_5\text{OH}$) were analytical reagent grade. ZnO sol was prepared by dissolving ZAD (22.5 g) and MEA (6.15 ml) in 2-methoxyethanol (200 ml) and refluxing at 70 °C under vigorous stirring for 60 min. The resultant solution was left standing at room temperature for a certain time for deep hydrolysis reaction and aging. The nano-sized ZnO films were prepared by dip-coating process: firstly, aluminum foil substrates were pretreated by dipping in basic degreased reagent for 30 min, then washing with distilled water for several times, subsequently drying in oven at 350 °C for 2 h. Secondly, the precursor sols were deposited on the aluminum foil substrates for 2 min and dried in the air for 10 min. As-synthesized films were dried at 100 °C for 30 min and further treated at 500 °C for 120 min.

2.2. Characterization of photocatalysts

The thermal-decomposition behavior of the ZnO sols is monitored using a TG–DSC instrument (thermogravimetry–differential scanning calorimetry, STA449C, Jupiter, Netzsch, Germany). An X-ray diffractometer (D/max-III A, Japan) was used for XRD (X-ray diffraction) analysis. The radiation source was Cu K α , and the applied current and voltage were 30 mA and 30 kV, respectively. During the analysis the sample was scanned from 20 to 70°. The surface morphology was characterized with a SEM (scanning electron microscopy, LEO1530VP, LEO Company) at an acceleration voltage of 10 kV and an AFM (atom force microscope, CSPM3000, BenYuan Nano Apparatus Ltd., China). The UV–vis spectra were obtained from a Hitachi U-3010 spectrophotometer equipped with an integrating sphere assembly, using BaSO₄ as a reference to measure all the samples.

2.3. Photocatalytic reaction

Photocatalytic activities of the aluminum foil-supported ZnO thin films were assessed by the photodegradation of phenol in aqueous suspension. The photocatalytic reaction was conducted in cylindrical glass vessel with XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant), which configures with several accessories such as magnetic force stirrer, quartz cool trap, condensation tube, which can keep the reaction temperature steady and prevent the evaporation of water. 1000 W Xe lamp was also used as visible light source, which mainly emits visible light in the range of 400–800 nm. A water filter mounted on the lamp housing to eliminate infrared radiation. A cutoff filter was placed after the water filter to completely remove the UV portion of the radiation (<420 nm) and to ensure that photocatalysis is achieved by visible light wavelengths only. The solution was stirred magnetically with reaction temperature at 30 °C.

The phenol aqueous solution was made from analytical pure grade chemical in distilled water. Two pieces of ZnO/Al thin film (total efficient irradiation area of film 400 cm², about 30 mg ZnO) as photocatalyst was suspended in 20 mg L⁻¹ phenol aqueous solutions (500 mL). All experiments were conducted in presence of O₂ using well-stirred oxygen-equilibrated suspensions. At regular intervals, a 15 ml of the suspension was withdrawn and filtered through a 0.2 μm membrane filter. Subsequently, the filtrate was analyzed for the absorbance of remaining pollutants by Hitachi U-3010 spectrophotometer and total organic carbon (TOC) by 1020A (OI Analytical Company). Blank tests of adsorption and photolysis were also carried out in the same condition as photocatalysis experiments.

3. Results and discussion

3.1. Structure characterization

The thermal analysis of the ZnO sols was carried out with TG–DSC in the temperature range of 30–700 °C at heating rate of 10 °C/min under nitrogen atmosphere (shown in Fig. 1). The solute in as-formed sol was confirmed to be Zn-oxo acetate colloidal particle by FT-IR spectrometer in the reported literature [17]. The DSC curve shows a large and sharp endothermic peak at 130.6 °C, corresponding to the evaporation of methyl glycol. The peak temperature is a little higher than the boiling point of pure methyl glycol (between 122 and 125 °C) due to the colligative property. The TG curve in Fig. 1 can be divided into five stages. The first stage is from room temperature to 110 °C, a mass loss of about 5.69% is observed, which is attributed to the evaporation of low boiling point organics substance and water. The largest weight loss (78.54%) is from the temperature range from 110 to 150 °C. This could be a result of the evaporation of methyl glycol. In the third stage from 150 to 210 °C, the mass loss is about 3.73%, this can be ascribed to the evaporation or decomposition of higher boiling point organic compounds mostly monoethanolamine. Weight loss of the fourth stage from 210 to 250 °C is up to 4.93% mainly owing to the desorption and decomposition of acetate group from Zn-oxo acetate colloidal particles. The last stage from 250 to 700 °C with a mass loss of 2.13% is as a result of the combustion of organic residues. On the basis of the above results, the whole mass loss ratio is about 95%, which corresponds with the concentration of the ZnO sol (4 wt.%). From the whole TG curve, there is little weight loss from 400 to 700 °C. Therefore, pure ZnO thin film can be obtained by heating the subsequent samples to 500 °C.

The phase behavior of aluminum foil-supported ZnO thin film was observed by XRD (Fig. 2). The XRD pattern of ZnO/Al thin film shows the presence of peaks ($2\theta = 31.86, 34.56, \text{ and } 36.34^\circ$), which was regarded as an attributive indicator of hexagonal zinc oxide. The other five peaks ($2\theta = 38.54, 44.78, 65.12, 78.26, 99.12^\circ$), which is an indicator of aluminum, show much higher intensity than peaks of ZnO due to high content of aluminum and low thickness of ZnO thin film.

The scanning electron microscopy images of ZnO/Al thin films are shown in Fig. 3(a). It is indicated that the ZnO/Al thin film is porous and the grain average size of ZnO is 50 nm. Fig. 3(b) shows that the measured surface

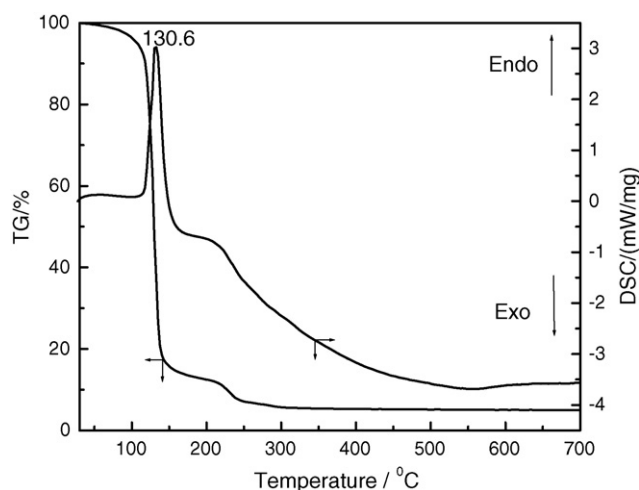


Fig. 1. TG–DSC curves of ZnO sols.

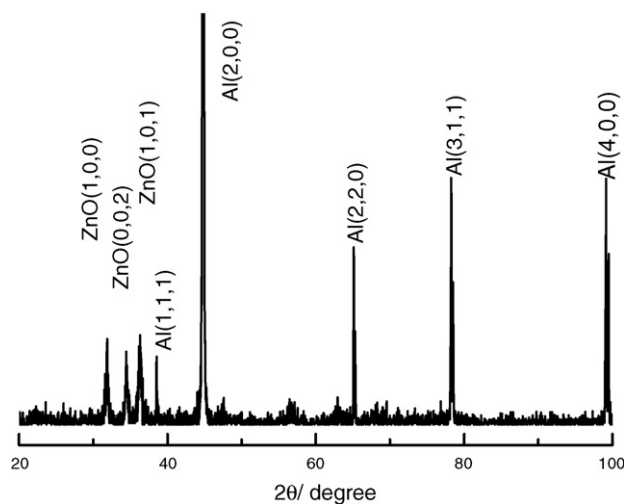


Fig. 2. XRD pattern of aluminum foil-supported ZnO thin film.

morphology (3D mode) of ZnO/Al thin film by AFM is in acceptable agreement with Fig. 3(a) by SEM. Based on statistics of 1543 particles, the average diameter of ZnO particles and the average height of film are 52.2 nm and 53.6 nm, respectively. The section of this ZnO/Al thin film is also characterized by means of SEM, the testing result shows the average thickness of film is 55 nm. It is indicated that the average thickness of film is consistent with of average diameter of ZnO particles, and the thin film is formed by a layer of ZnO nano-sized particles.

Fig. 4 shows that the aluminum foil has little absorption both in ultraviolet range and visible range from 200 to 800 nm, while the absorption spectra of ZnO/Al thin film shows strong absorption in ultraviolet range from 200 to 400 nm with an absorption edge at about 380 nm, which can be ascribed to the fundamental absorption of ZnO. TiO₂ (P25) has strong absorption in ultraviolet range as ZnO/Al thin film; however, on the visible range from 450 to 800 nm, ZnO/Al thin film shows stronger photoabsorption than TiO₂ nano-powder.

3.2. Photocatalytic activity

Phenol is widely distributed as environmental pollutants due to their common presence in the effluents of many industrial processes, including oil refineries, petrochemical plants, ceramic plants, steel plants, coal conversion processes and phenolic resin industries. Wastewater containing phenols need careful treatment before discharge into the receiving body of waters. So far there were only few reports of phenol degradation under visible light [18–20]. However, the efficiency is limited by the light absorption characteristics of the TiO₂-based photocatalysts. It is in urgent need to develop a new visible-driven photocatalyst with higher activity. Phenol can only absorb ultraviolet light with a absorption peak on 270 nm range from 240 to 280 nm, this may be a reason that phenol can not be photolyzed under visible light irradiation. It is stable to visible and near UV light and provides a useful probe for photoredox reaction.

Adsorption-time curves of phenol in Fig. 5(1) shows less than 3% of phenol is adsorbed on ZnO thin film surface in the same condition as photocatalysis but without irradiation. The photolysis performance of phenol is shown in Fig. 5(2), which shows that phenol is hardly degraded under visible light irradiation without catalyst, only 2% of total organic carbon (TOC) is removed after 3 h irradiation. After photocatalysis time of 3 h, more than 40% of the initial phenol was totally mineralized (i.e. to CO₂ and H₂O; see Fig. 5(4) TOC curve). Surprisingly, degradation rate of phenol denoted with method of absorbance ($1 - A/A_0$) is lower than with method of total organic carbon ($1 - \text{TOC}/\text{TOC}_0$). In fact, many references [21,22] reported hydroquinone, *p*-benzoquinone as main reaction intermediates in the photocatalysis of phenol under ultraviolet. In this study, the aliquot was taken at 30 min interval, the compounds of 1,2- and 1,4-hydroxybenzenes and *p*-benzoquinone were also detected in the course of the photocatalytic reaction by GC–MS. We think that the photocatalytic degradation pathway of phenol under visible light irradiation is the same as

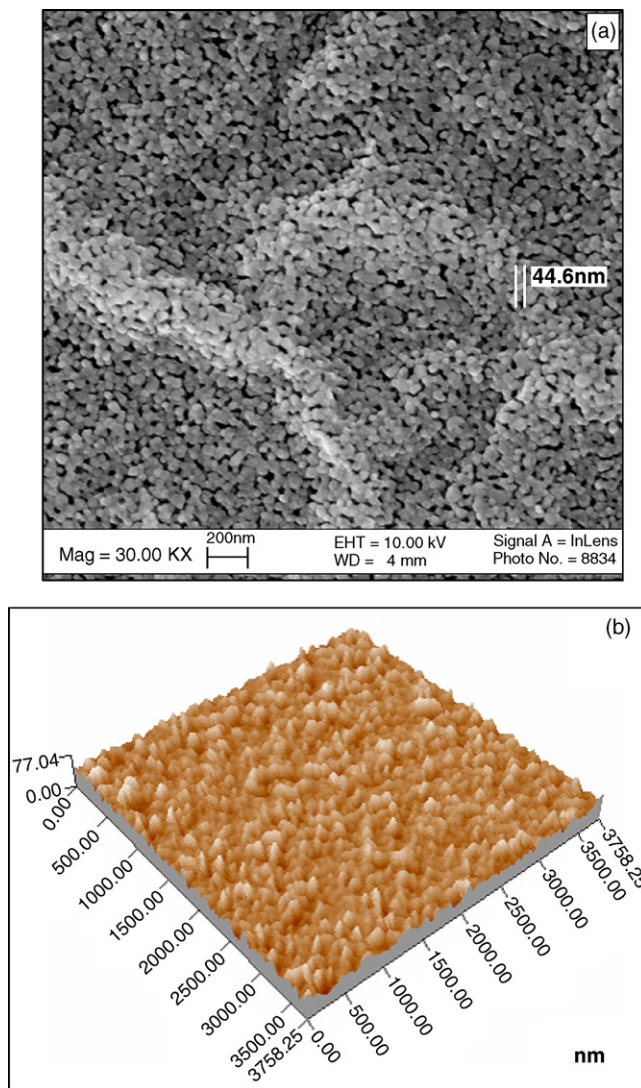


Fig. 3. SEM photograph (a) and AFM photograph (b) of nano-ZnO thin film.

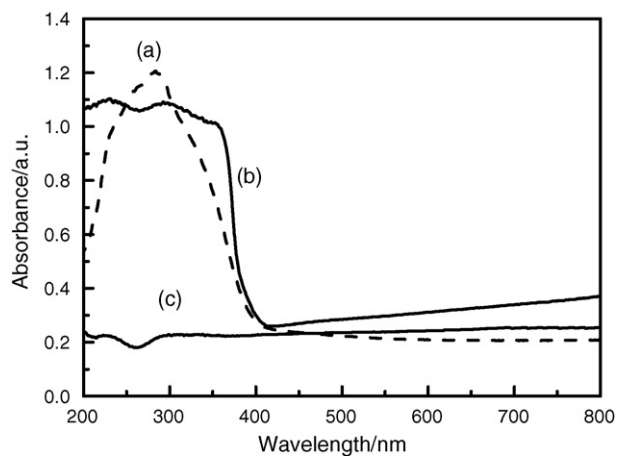


Fig. 4. The UV-vis spectra of P25-TiO₂ (a), ZnO/Al thin film (b) and aluminum foil (c).

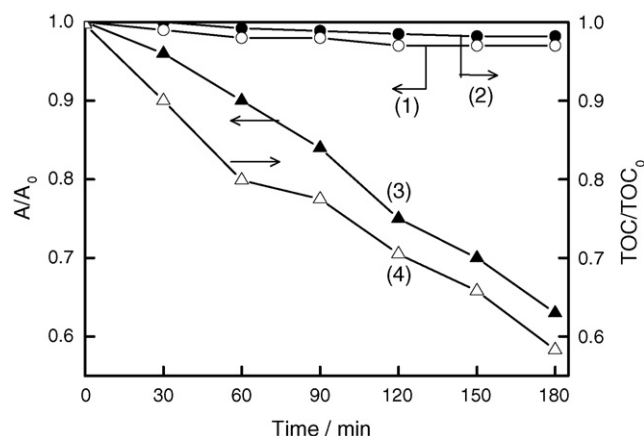


Fig. 5. The curves of phenol adsorption (1) and photocatalysis (3) denoted with A/A_0 ; and the curves of phenol photolysis (2) and photocatalysis (4) denoted with TOC/TOC_0 .

under ultraviolet [21]. It is very clear that the absorbance of reaction intermediates of hydroxybenzenes is higher than phenol at around 250–270 nm. The absorbance detected is a multiplex effect of phenol and reaction intermediates, and the absorption peak is also shifted from 270 to 265 nm after 3 h photocatalysis. It is indicated that the absorbance detected cannot denote the concentration of phenol in the course of the photocatalytic reaction; therefore, the degradation rate of phenol denoted with method of absorbance is not reasonable. From TOC curve, we can see that 42% of phenol was totally destructed after photocatalysis time of 3 h. Indeed, the disappearance of phenol itself was more than 37% ($1 - A/A_0$), about 55% of substrate was photocatalytically oxidized after 3 h irradiation. This is to say that about 13% of initial phenol was not totally mineralized; it was converted into other intermediates. In order to rationally compare photocatalytic activity, 60 mg P25–TiO₂ nano-powder (the mass of ZnO supported on two pieces of thin film is about 30 mg) as photocatalyst was used to degrade phenol (20 mg L⁻¹, 500 mL) in the same photocatalysis condition. After photocatalysis time of 3 h, only 5% of the initial phenol was totally mineralized. It is indicated that phenol is hardly degraded under visible light irradiation with pure TiO₂ catalyst. These ZnO/Al thin films were recovered by washing and drying for further reaction. It was found that the catalytic activity for the degradation of phenol remained similar, even after the ZnO thin film had been recycled for another third time, which was 90% of the first activity. The results suggest that the ZnO-supported commercial aluminum foil is a promising and efficient thin film catalyst to degrade organic pollutants under visible light irradiation.

4. Conclusions

The transparent ZnO sols have been prepared by sol–gel method with methyl glycol as solvent and a novel ZnO/Al thin film catalyst has been prepared by dip-coating method with a commercial aluminum foil as substrate. The film was characterized by means of TG–DSC, XRD, UV–vis, SEM and AFM. It is showed that the thin film is porous, which is formed by a layer of ZnO nano-sized particles with average diameter of 52.2 nm. ZnO/Al thin film shows stronger photoabsorption than TiO₂ (P25) nano-powder in the visible range from 450 to 800 nm. The ZnO/Al films have been employed in photocatalytic degradation of wastewater with phenol. The photocatalytic degradation pathway of phenol under visible light irradiation is the same as under ultraviolet. Under the initial concentration of 20 mg/L phenol solution (500 mL) and reaction time of 3 h, more than 40% of the initial phenol was totally mineralized using two pieces of ZnO/Al thin film as photocatalyst with an efficient irradiation area of 400 cm². The ZnO-supported commercial aluminum foil is a promising and efficient catalyst to degrade organic pollutants under visible light irradiation.

Acknowledgements

The authors thank the Guangdong Provincial Natural Science Foundation of China (No. 05006553) and the Guangdong Provincial Science and Technology Project of China (No. 2005A10702002) for financial support.

References

- [1] Z. Aksu, *Process Biochem.* 40 (2005) 997.
- [2] A. Katsoyiannis, C. Samara, *Environ. Res.* 97 (2005) 245.
- [3] G.H. Chen, *Sep. Purif. Technol.* 38 (2004) 11.
- [4] D. Rajkumar, K. Palanivelu, *J. Hazard. Mater.* 113 (2004) 123.
- [5] A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gómez-Gómez, F. Máximo-Martin, A.M. Hidalgo-Montesinos, *Desalination* 155 (2003) 101.
- [6] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [7] F. Peng, Y.Q. Ren, *Chin. J. Catal.* 24 (2003) 243.
- [8] C.H. Kwon, H. Shin, J.H. Kim, W.S. Choi, K.H. Yoon, *Mater. Chem. Phys.* 86 (2004) 78.
- [9] S. Sakthivel, H. Kisch, *ChemPhysChem* 4 (2003) 487.
- [10] H. Luo, T. Takata, Y. Lee, J. Zhao, K. Domen, Y. Yan, *Chem. Mater.* 16 (2004) 846.
- [11] S. Malato, J. Blanco, A. Vidal, C. Richter, *Appl. Catal. B: Environ.* 37 (2002) 1.
- [12] R. Asahi, T. Morikawa, T. Ohwaki, *Science* 293 (2001) 269.
- [13] M.C. Yeber, J. Rodriguez, J. Freer, N. Duran, H.D. Mansilla, *Chemosphere* 41 (2000) 1193.
- [14] C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Duran, N. Nagata, P. Peralta-Zamora, *Chemosphere* 40 (2000) 433.
- [15] B. Dindar, S. Icli, *J. Photochem. Photobiol. A: Chem.* 140 (2001) 263.
- [16] K. Iketani, R.D. Sun, M. Toki, K. Hirota, O. Yamaguchi, *Mater. Sci. Eng. B* 108 (2004) 187.
- [17] L. Znaidi, G.J.A.A. Soler Illia, S. Benyahia, C. Sanchez, A.V. Kanaev, *Thin Solid Films* 428 (2003) 257.
- [18] V. Iliev, *J. Photochem. Photobiol. A: Chem.* 151 (2002) 195.
- [19] E. Pepe, O. Abbas, C. Rebufa, M. Simon, S. Lacombe, M. Julliard, *J. Photochem. Photobiol. A: Chem.* 170 (2005) 143.
- [20] S. Kim, W. Choi, *J. Phys. Chem. B* 109 (2005) 5143.
- [21] A. Sobczynski, L. Duczmal, W. Zmudzinski, *J. Mol. Catal. A: Chem.* 213 (2004) 225.
- [22] B. Sun, A.V. Vorontsov, P.G. Smirniotis, *Langmuir* 19 (2003) 3151.