PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: “Jovan” Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: “Jovan”

200 - *Coppy priting*

PHYSICAL CHEMISTRY 2014

12th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences

Faculty of Physical Chemistry, University of Belgrade, Serbia

Institute of Chemistry Technology and Metallurgy, University of Belgrade, Serbia

Vinča Institute, University of Belgrade, Serbia

Institute of General and Physical Chemistry, Serbia

Faculty of Pharmacy, University of Belgrade, Serbia

PHOTOCATALYTIC ACTIVITY OF PEG-MODIFIED CATALYSTS

D. Lončarević[1], J. Dostanić[1] and A. Radosavljević-Mihajlović[2]

[1]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia. (dloncarevic@nanosys.ihtm.bg.ac.rs)*
[2]*University of Belgrade, Institute of Nuclear Sciences Vinča, Laboratory for Material Science, P.O. Box 522, Belgrade, Serbia.*

ABSTRACT

This work is focused on the influence of polyethylene glycol (PEG) on structural, textural and photocatalytic properties of titanium dioxide (TiO_2) catalyst. Catalysts were synthesized by sol-gel method using PEG with different molecular weight (600 and 10000) as pore generating agent. The results showed that PEG enhances not only porous structure but also change anatase to rutile ratio. The photocatalytic activity of the synthesized catalyst was measured by decomposition of phenol. The order of catalyst photoactivity was: TiO_2/P600>TiO_2/P10000>TiO_2.The difference in catalyst photoactivity is attributed to their surface area and anatase fraction, rather then pore size.

INTRODUCTION

In the last decades photocatalysis became attractive method for the treatment of air and water pollution. The appliance of nanosized metal oxides, typically semiconductors, as photocatalyst has been studied intensively [1]. TiO_2 generate special interest as photocatalyst, due to its high photocatalytic activity, non-toxicity, chemical stability and low cost [2]. Among three distinct crystallographic forms (anatase, rutile and brookite), anatase is considered to be the most active phase, due to the lowest rate of electron/hole recombination [3]. Textural properties such as specific surface area, porosity and mean pore size are also of great importance and can be decisive factor for photocatalytic application [4]. The highly porous structure of catalyst is an imperative, since it offers a much larger number of catalytic sites than a dense structure.

Sol-gel method is one of the most used methods for the synthesis of solid inorganic materials [5]. The hydrolysis and polycondensation rate strongly affects the structure and properties of TiO_2. One possibility to restrain the rapid hydrolysis and polycondensation is to use different organic additives during catalyst preparation [6]. Condensation process is accomplished by gelization, which is followed by calcination. Since calcination leads to decrease in catalyst porosity, organic templates, such as PEG [7] etc., are often used in order to retain the porous structure of the catalyst after calcinations.
This study investigates the influence of textural and structural parameters on photocatalytic activity of PEG-modified TiO_2 catalyst.

EXPERIMENTAL

TiO_2 catalysts were synthesized by sol-gel process. Briefly, 3.73 mL of titanium-tetraisopropoxide was dissolved in 10 mL of anhydrous ethanol and 1.15 mL of diethanol amine at room temperature (solution A). Meanwhile, 35 mL of anhydrous ethanol was mixed with 3.75 mL of water (solution B). Solution A was subsequently added dropwise to solution B within 20 min. After that, 1.0 g of PEG was added to solution and stirred for another 40 min. The stabilized sol was aged for another 12 h at room temperature. The formed gel was then dried in an oven for 12 h at temperature of 80 ºC, and calcined at 550 ºC for 4 h. The control sample was prepared without the use of the template by the same sol-gel method.
Nitrogen adsorption-desorption isotherms were determined using nitrogen physisorption at -196 ºC. Specific surface area (S_{BET}) and pore size (D_{max}) of the samples was calculated from the nitrogen adsorption isotherms according to the BET and BJH methods, respectively. Pore volume (V_{pore}) was determined by mercury intrusion porosimetry. Powder X-Ray diffraction patterns were measured on a diffractometer using Cu-Kα radiation (λ = 1.5418 Å).
Photocatalytic tests were performed in an open cylindrical thermostated Pyrex cell (250 mL). The irradiation was performed using Osram Ultra Vitalux lamp (300 W), housed 50 cm above the top surface of the dye solution. Photocatalytic activity of catalysts was measured by decomposition of phenol in aqueous solution. Applied conditions used during photocatalytic tests were: solution volume: 150 mL, initial phenol concentration: 2.8×10^{-5} mol/L, T: 30 ºC, catalyst mass: 1.5 g. The concentration of phenol during catalytic tests was determined using UV-Vis spectrophotometer. The phenol removal, i.e. conversion efficiency, X, was determined using equation $X=(C_0-C)/C_0$, where C_0 is the initial phenol concentration and C is the phenol concentration for the specified time.

RESULTS AND DISCUSSION

Table 1 presents textural and structural of the prepared catalyst. It can be seen that PEG-modified samples have noticeably larger pore volume and surface area than unmodified sample. The largest pore volume and specific surface is obtained for the sample TiO_2/P600, while sample TiO_2/P10000 has the largest pore diameter.

Table 1. Textural and structural properties of TiO_2 samples

Sample	S_{BET}	D_{max}	V_{pore}	Fraction of Anatase	Fraction of Rutile
	[m^2/g]	[nm]	[mm^3/g]	[%]	
TiO_2	4.8	16.4	13	17.2	82.8
TiO_2/P600	28.3	15.7	125	74.2	25.8
TiO_2/P10000	14.4	18.3	97	45.8	54.2

Increasing molecular weight of PEG molecules led to higher pore diameter and smaller surface area. However, the samples didn't have the same porosity as it was expected. The difference in porosity indicates different stability of porous network during thermal treatment, which is a consequence of pore shrinkage.

The calculated weight fractions of the anatase and rutile phases for samples are presented in Table 1. The maximum rutile fraction was observed for the unmodified sample TiO_2, while PEG modified sample contain lower fraction of rutile phase. Among modified samples, sample TiO_2/P600 contain higher fraction of anatase phase then sample TiO_2/P10000.

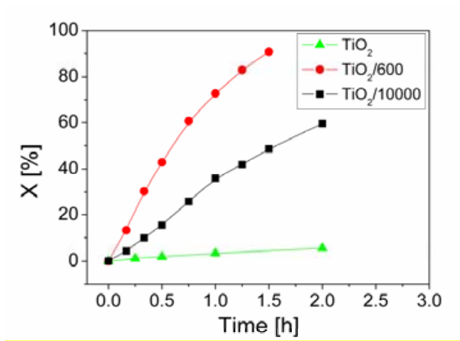

Figure 1. Photodegradation of phenol.

The photocatalytic degradation of phenol was presented in Fig. 1. The results clearly indicate that PEG-modified samples exhibit significantly higher activity compared to the activity of the control unmodified sample. The increased activity of PEG-modified samples can be attributed to their higher surface area, pore volume and pore size. In addition, higher fraction of active anatase phase of PEG-modified samples additionally enhances their activity. Among modified samples, the sample TiO_2/P600 displayed significantly higher activity compared to the sample TiO_2/P10000. The obtained results indicate that specific surface area and anatase to rutile ratio contribute more in determining photocatalytic efficiency, then pore size.

CONCLUSION

The results of this study illustrate the influence of PEG on textural, structural and photocatalytic properties of TiO_2 materials. The decomposition of PEG during thermal treatment led to generation of porous strucuture, thus improving the textural properties of samples. Also, PEG introduction changes anatase to rutile ratio. PEG-modified samples displayed significantly higher activity then unmodified sample. Among modified samples TiO_2/P600 showed higher activity then TiO_2/P10000. The difference in activity is attributed to the surface area and anatase to rutile ratio. Variation in pore size are found not to be decisive factor for photcatalytic efficiency.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects No. III 45001).

REFERENCES

[1] D. A. Tryk, A. Fujishima, K. Honda, Electrochimica Acta, 2000, 45, 2363-2376.
[2] D. Beydoun, R. Amal, G. Low, S. McEvoy, Journal of Nanopartarticle Research, 1999, 571, 439-458.
[3] I. K. Konstantinou, T. A. Albanis, Applied Catalysis, B: Environmental, 2004, 49, 1-14.
[4] Y. Chen, D. D. Dionysiou, Applied Catalysis B: Environmental, 2006, 69, 24-33.
[5] C. Su, B-Y. Hong, C-M. Tseng, Catalysis Today, 2004, 96, 119-126.
[6] S. J. Bu, Z. G. Jin, X. X. Liu, L. R. Yang, Z. J. Cheng, Journal of the European Ceramic Society, 2005, 25, 673-679.
[7] B. Guo, Z. Liu, L. Hong, H. Jang, Surface and Coatings Technology, 2005, 198, 24-29.