ZINC OXIDE NANOPARTICLES IMMOBILIZED ON ORDERED (SBA-15) AND DISORDERED (KIL-2) MESOPOROUS SILICATE SUPPORTS

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ABSTRACT

ZnO is a well-known photocatalyst for the degradation of dyes in wastewater treatment by using UV and solar light. However, the recycling of ZnO semiconductor nanoparticles presents a problem. We tried to solve this problem by immobilizing ZnO nanoparticles on different porous silicate supports. Mesoporous ordered silicate SBA-15 and disordered silicate KIL-2 have already been found appropriate for host matrices for TiO_2 nanoparticles. In this contribution we present the immobilization of ZnO nanoparticles on porous silicate supports for the photocatalytic degradation of dyes. We have deposited ZnO nanoparticles on SBA-15 and KIL-2 porous matrices with various Zn/Si ratios by using a Schlenk-line. The composites were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption. The photocatalytic activity of these composite materials for the degradation of organic dyes will be tested in a laboratory reactor.

Keywords: ZnO nanoparticles, mesoporous silicate supports, SBA-15, KIL-2, photocatalysis, dye degradation.

INTRODUCTION

With industrialization and population growth, the environmental contamination caused by organic pollutants is becoming an overwhelming problem all over the world [1]. Large amounts of dyes are annually produced and applied in different industries including textile, cosmetic, paper and leather industries. More than 15% of dyes used in the industrial processes are later found in wastewaters. In the last decade advanced oxidation processes (AOPs) have been used for wastewater treatment. AOPs are based on the activity of very reactive species such as hydroxyl radicals which quickly and none selectively oxidize a broad range of organic pollutants [2].

ZnO is the well-known photocatalyst for the degradation of various organic dyes in wastewater treatment. With decrease of particle size of the ZnO to nanoscale, the surface area and efficiency of catalyst increase. The challenge remaining is recycling of used photocatalyst. One of the possible solutions is the immobilization of ZnO nanoparticles on mesoporous silicate supports [3].

In this contribution we present characterization of ZnO nanoparticles immobilized on disordered (KIL-2) and ordered (SBA-15) mesoporous silicate supports.

EXPERIMENTAL

Mesoporous disordered silicate KIL-2 [3] was prepared by two-step synthesis in molar ratio 1TEOS : 0.5TEA : 0.1TEAOH : $11H_2O$. In the first step tetraorthosilicate (TEOS 98%, Acros) and triethanolamine (TEA 99%, Fluka) were stirred for 30 minutes. Finally demineralized water was added to the above mixture, followed by the addition of tetraethyammonium hydroxide (TEAOH 20%, Acros). The solution was mixed with a

magnetic stirrer to obtain a homogeneous gel. The final gel was aged overnight at room temperature and then dried in an oven at 50°C for 24h. In the second step the gel was solvothermally treated in ethanol in a Teflon-lined stainless autoclave at 150°C for 48h. Removal of the template was performed by calcination at 500°C for 10h in the flow of air.

Mesoporous ordered silicate SBA-15 [4] was prepared by hydrothermally synthesis in molar ratio 1TEOS : 0.017P123 : 5.85HCl : 190H_2O. The structure-directing agents Pluronic P123 triblock copolymer (P123, Aldrich) was dissolved in solution of water and HCl (HCl 37%, Merck). Tetraorthosilicate (TEOS 98%, Acros) was added to homogeneous solution under stirring at 40°C for 8h. Then the gel was aged at 80°C for 16h without stirring. The final gel was heated in a Teflon-lined stainless autoclave at 100°C for 24h. Removal of the template was performed by calcination at 500°C for 6h in the flow of air.

Finally, ZnO nanoparticles prepared according to literature data [2,3] were immobilized on before mentioned mesoporous silicate supports. The composites were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and nitrogen adsorption.

RESULTS AND DISCUSSION

The SEM images of disordered mesoporous silicate support KIL-2, ordered mesoporous silicate support SBA-15 and their composites are shown in Figs.1-4. SEM images suggest that the morphology of composites does not change compared to KIL-2 and SBA-15.

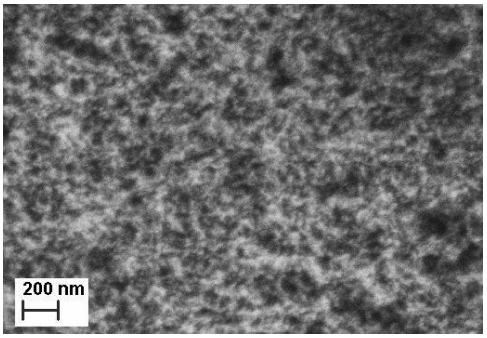

Figure 1. SEM image of KIL-2.

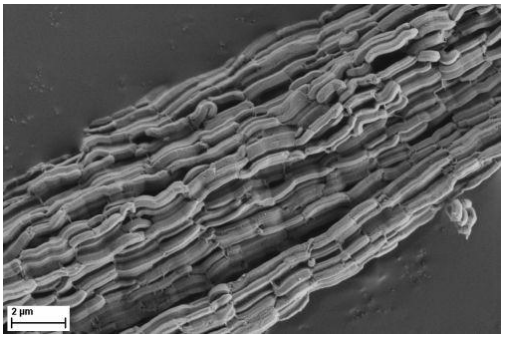

Figure 3. SEM image of SBA-15.

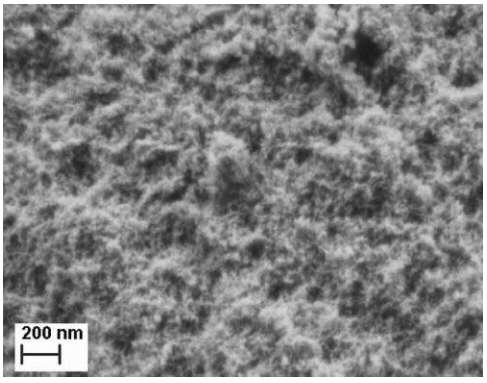

Figure 2. SEM image of composite KIL-2/ZnO-0.25 .

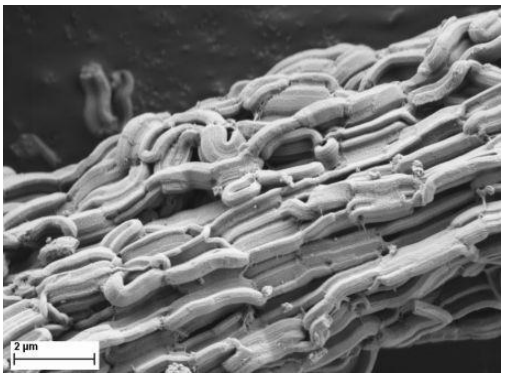

Figure 4. SEM image of composite SBA-15/ZnO-0.25.

The low-angle powder XRD patterns of KIL-2 and SBA-15 indicate that the KIL-2 has a disordered mesoporous structure while the SBA-15 has an ordered hexagonal pore

arrangement (not shown). The XRD patterns of composites (Fig.5 and Fig.6) recorded at the wide-angle range (5° - 60°) confirm that ZnO nanoparticles are present in both composites.

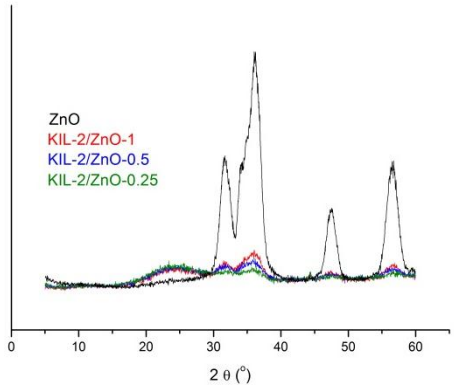

Figure 5. XRD patterns of ZnO and composites KIL-2/ZnO.

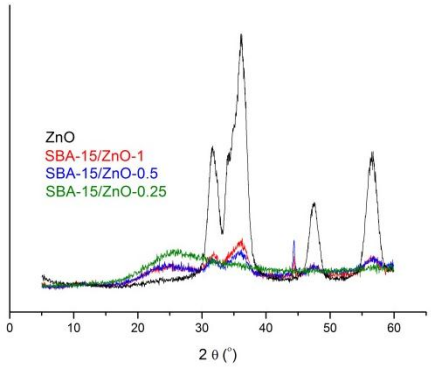

Figure 6. XRD patterns of ZnO and composites SBA-15/ZnO.

Nitrogen sorption isotherms of mesoporous silicate support (KIL-2) and composites are shown in Fig.7a. KIL-2 sample exhibited adsorption isotherm typical for KIL-2 silicate [3]. The adsorption and desorption branches are almost vertical and nearly parallel, indicating on the isotherm with uniformly sized pores filling and emptying in a narrow pressure range. It can clearly be observed that the presence of ZnO on KIL-2 support leads to a marked change in the shape of the hysteresis loop. The hysteresis loop of all samples is less intensive and is closing down at lower p/p_o values in comparison to the original support, which indicates that the pores are partially narrowed with ZnO nanoparticles.

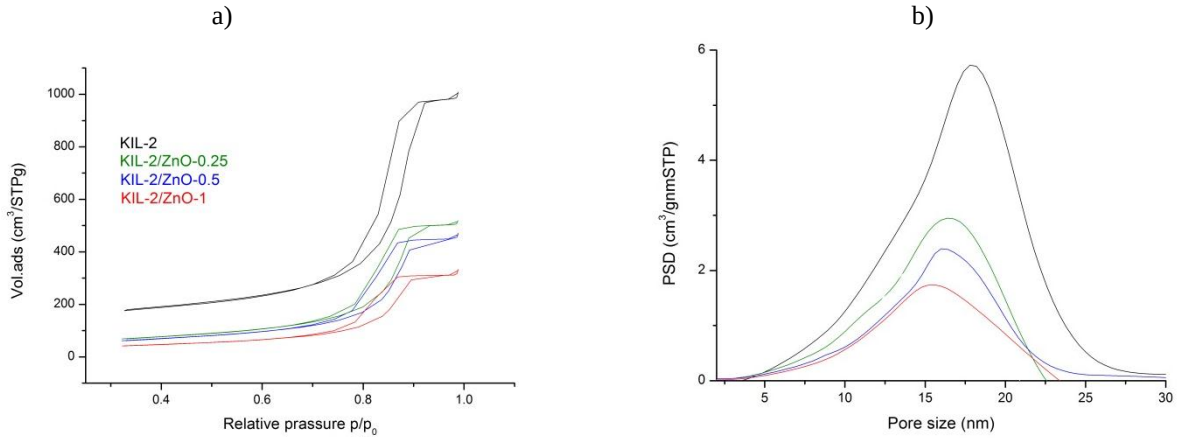

Figure 7. The nitrogen adsorption isotherms (a) and pore distribution of KIL-2 and comoposites (b).

Pore size distribution of the different mesoporous materials has been determined using the BJH model [5] widely used for this type of samples. The pore size distributions are determined from adsorption isotherms. The maximum characteristic to open mesopores of KIL-2 (Fig.7b) is the most intense and broad. The average pore diameter is 17.9 nm. The maxima characteristic for narrowed pores due to ZnO plugs shift to lower pore size value (15.4 nm) in all samples. Maxima are more narrow and intensive with higher amounts of ZnO (Fig.7b).

SBA-15 sample exhibits sorption isotherm with two-step desorption, which is typical for plugged hexagonal templated silica like material (PHTS) (Fig.8a). Plugged hexagonal

templated silica has the same 2D hexagonal symmetry as SBA-15 but some of its cylindrical mesopores have internal porous plugs, while others are open as inferred from gas adsorption-desorption data. The first-step on the desorption branch (Fig. 8a) is similar with the desorption in pure SBA-15 and is assigned to the desorption of N_2 from the open pores; the second desorption step can be attributed to the nanoparticles (plugs) within the mesopores (the narrowed mesopores). The second-step on the desorption branch indicates the existence of plugged mesopores. The presence of ZnO into SBA-15 changes the shape of the hysteresis loop. The hysteresis loop of all samples is closing down at lower relative pressure values in comparison to the original support, which indicates that the pores are partially narrowed with ZnO nanoparticles. The increase of the amount of the deposited ZnO nanoparticles on SBA-15 not only led to a decreased mesopore volume, but also resulted in an appreciable widening and tailing of hysteresis loops and in a two-step desorption, thus evidencing the PHTS like material. The maximum characteristic to open mesopores of SBA-15 (Fig.8b) is the most intense and shows the average pore diameter of 10.0 nm. The maxima characteristic for narrowed pores due to ZnO plugs shift to lower pore size value (7.3 nm) in all samples. Maxima are broader and less intensive with higher amounts of ZnO (Fig. 8b).

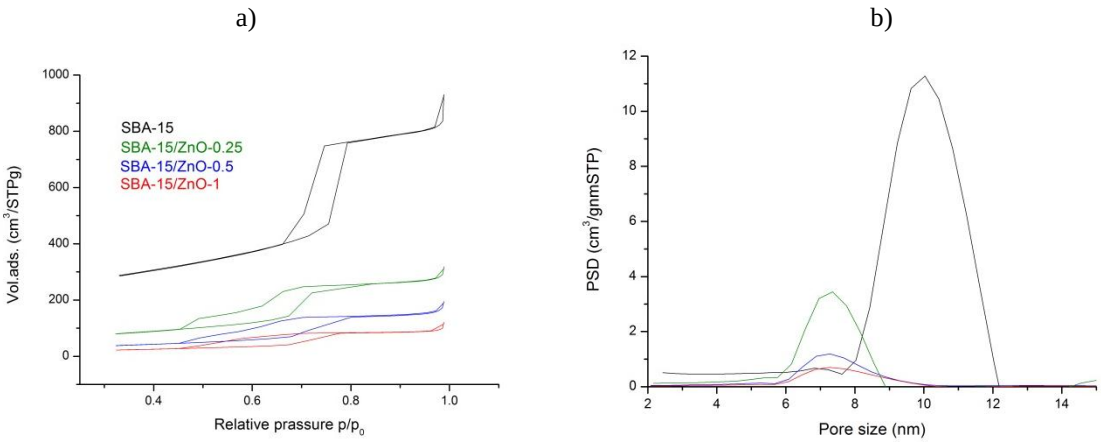

Figure 8. The nitrogen adsorption isotherms (a) and pore distribution of SBA-15 and comoposites (b).

CONCLUSION

We have successfully immobilized ZnO nanoparticles on the disordered mesoporous silicate support KIL-2 and ordered mesoporous silicate support SBA-15 with various Zn/Si ratio. These composites will be tested in photocatalytic reactions for the degradation of organic dyes.

REFERENCES

[1] C. Chen, W. Ma. and J. Zhao, *Chem. Soc. Rev.*, 2010, **39**, 4206-4219.
[2] M. Tashibi, PhD thesis, University of Nova Gorica, 2010.
[3] N. N. Tušar, A. Ristić, G. Mali, M. Mazaj, I. Arčon, D. Arčon, V. Kaučič and N. Z. Logar, *Chem. Eur. J.*, 2010, **16**, 5783-5793.
[4] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, J. *Am. Chem. Soc.*, 1998, **120**, 6024-6036.
[5] W.W. Lukes, P.Schmidt-Winkl, D. Zhao, J. Feng and G.D. Stucky, *Langmuir*, 1999, **15**, 5403.