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THE INFLUENCE OF THE HEAT TREATMENT ON THE PHOTOACTIVITY OF THE TiO_2-SiO_2 AEROGELS

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ABSTRACT. TiO_2-SiO_2 aerogels were prepared by sol-gel method followed by supercritical drying with liquid CO_2 and heat treatment. The structural and morphological particularities of the prepared TiO_2-SiO_2 aerogels were studied by means of X-ray diffraction and BET analysis. The photocatalytic activity of the TiO_2-SiO_2 aerogels was determined by monitoring the degradation rate of the salicylic acid. It was found that the efficiency of the TiO_2-SiO_2 catalyst strongly depends upon the heat treatment temperature and also on the silica content. The larger specific surface area has been achieved for the sample with the higher Si content. The heat treatment performed at 600^0C and 700^0C allowed the formation of anatase phase, as well as the meso- to micropore transformation. The TiO_2-SiO_2 (1:1 molar ratio) aerogel, heat treated at 500^0C has the highest photocatalytic activity.

KEYWORDS: TiO_2-SiO_2 aerogels, photocatalyst, sol-gel method, BET analysis, X-ray diffraction.

INTRODUCTION

TiO_2-SiO_2 binary materials have been attracting the interests of many researchers [1-8]. One of the outstanding features commonly attributed to the sol-gel processing of the multicomponent materials is the high degree of homogeneity at molecular scale. One of the most studied systems was TiO_2-SiO_2, especially because glasses of this system have a low thermal expansion coefficient and aerogels can be used as photocatalysts [9]. The photocatalytic activity of TiO_2-SiO_2 aerogels is due to their larger specific surface areas and higher porosities in comparison with conventional TiO_2-SiO_2. These solids combine the mechanical properties of silica with the chemical and catalytic properties of titania.

Anderson and Bard [10, 11] have demonstrated that a mixed oxide of TiO_2 and SiO_2 produced by a sol-gel method was a more efficient photocatalyst for the photodecomposition of rhodamine-6G than TiO_2 alone. The increase in efficiency was attributed to the presence of SiO_2 as adsorbent, which enhances the concentration of the organic material near to the TiO_2 sites.

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The heat treatment temperature influences the structure of the TiO_2-SiO_2 aerogels and also their photoactivity. Annealing at 500-600^{0}C determines the anatase phase obtaining, the structure of TiO_2 with the most intense photocatalytic activity. The aerogels annealed at temperatures above 700^{0}C contain rutil phase, which doesn't manifest photoactivity [12]. In contrast, Choi and coworkers [13] obtained TiO_2-SiO_2 aerogels which remain amorphous even after heat treatment at 1000^{0}C. This behavior is explained by the small amount and very good dispersion of TiO_2 (Si :Ti = 1:0.05 molar ratio) into SiO_2 network.

In this work, we prepared TiO_2-SiO_2 aerogels with different contents of Ti and Si, which are subsequently heat treated at different temperatures. Our interest was also focused on determining the photocatalytic activity of the prepared samples and on finding the role played by both the SiO_2 presence, besides TiO_2, and the heat treatment effect on the salicylic acid photodegradation rate. The photocatalytic activity of the as prepared aerogels in the salicylic acid decomposition process is influenced by the Si content and also by the heat treatment temperature.

EXPERIMENTAL PART

The sols were prepared from Ti(IV) isopropoxide (Merck), tetramethoxysilane (Merck), anhydrous ethanol (Fluka), water and nitric acid reagent (Aldrich). The molar ratio of reactants was: $[Ti/Si]:[H_2O] = 1:3.5$, $[Ti/Si]:[C_2H_5OH] = 1:23.33$, $[Ti/Si]:[HNO_3]= 1:0.08$.

The as prepared gels were kept for 4 weeks in closed vessels and than were dried using supercritical CO_2 in a SAMDRI – 790 A (Tousimis) critical point dryer. Annealing, at 500^{0}C, 600^{0}C and 700^{0}C for 2 h was performed to obtain crystalline phases of TiO_2 and to remove residues of organic substances.

The X-ray diffraction patterns were obtained using a standard BRUKER D8 Advance X-Ray Diffractometer, working at 45 kV and 30mA. The Cu K_α radiation, Ni filtered, was collimated with Soller slits. The data of the X-ray diffraction patterns were collected in a step-scanning mode with $\Delta 2\theta = 0.02^0$ steps. Pure silicon powder standard sample was used to correct the data for instrumental broadening.

The X-ray diffraction patterns were obtained also by using a standard DRON-3M powder diffractometer, working at 35 kV and 25 mA, and equipped with scintillation counter with single channel pulse height discriminator counting circuitry. The Co K_α (λCuK = 1.54178 Å) radiation, Fe filtered, was collimated with Soller slits. The data of the X-ray diffraction patterns were collected in a step-scanning mode with $\Delta 2\theta = 0.05^0$ steps and then transferred to a PC for processing.

The specific surface area of the as prepared samples was determined using Brunauer-Emmett-Teller (BET) method, in a partial pressure range of $0.05 < P/P_0 < 0.3$. Kripton adsorption was carried out at 77 K. Before each measurement, the samples were heat-cleaned at 333 K for 2h.

Studies of photocatalytic activity of the TiO_2-SiO_2 aerogels were performed measuring the degradation rate of salicylic acid. The decrease in time of the salicylic acid concentration (C_0 = 3,38 x 10^{-4} M) was measured by spectrophotometry (λ = 297 nm). The aerogels immersed in salicylic acid solution were irradiated with UV light. The experimental setup contains: a medium pressure Hg lamp (500 W) as UV source; polyethylene photochemical 8 ml capacity cell with quartz window (S=12 cm^2); working temperature: 20-22^{0}C, solution pH = 5.3. Before UV irradiation as well as before spectrophotometric measurements, the cell with the sample was kept in dark for 15 minutes in order to achieve the equilibrium of the adsorption-desorption process.

RESULTS AND DISCUSSION

In table 1 are presented the Ti composition, the specific surface area and the salicylic acid photodecomposition apparent rate constants of the TiO_2-SiO_2 aerogels.

The specific BET surface area decreases with heat treatment temperature, due to the meso- to micropores transformation. For aerogels heat treated at 500^{0}C, the specific BET surface area increases with Si content. This behavior can be explained by the high porosity of silica. The salicylic acid photodecomposition apparent rate constants decreased with heat treatment temperature, with exception of A1 sample. On this aerogel type, thermal treated at 500^{0}C, the rate constant is much smaller than the one obtained for the aerogels heat treated at 600 and 700^{0}C. This behavior could be explained by the amorphous structure of this sample.

In figure 1 are presented the X-ray diffraction patterns obtained using Co radiation and Fe filter, of the aerogels heat treated at 600 and 700^{0}C.The greater rate constant value observed for the A1 (600) sample is due to the formation of the anatase phase (figure 1), which has photocatalytic activity [14]. The very small rate constant value of the A1 (700) sample is mainly caused by the change in the structure from meso- to micropores. The microporous structure inhibits the diffusion of various gaseous reactants and products during photocatalytic reaction, and those decrease the photocatalytic activity.

Table 1.

The Ti molar percentage content of the TiO_2-SiO_2 aerogels, the specific surface area and the salicylic acid photodecomposition apparent rate constants

	Sample cod	**Sample type**	**Ti [% mol.]**	**S_{BET} [m^2/g]**	**k_{app} x 10^{-3} [min^{-1}]**
Sample A 1	A 1 (500)	TiO_2-SiO_2 heat treated for 2 h, at 500^0C	75	62	0.3481
	A 1 (600)	TiO_2-SiO_2 heat treated for 2 h, at 600^0C	75	52	1.13
	A 1 (700)	TiO_2-SiO_2 heat treated for 2 h, at 700^0C	75	44	0.2152
Sample A 2	A 2 (500)	TiO_2-SiO_2 heat treated for 2 h, at 500^0C	50	384	3.97
	A 2 (600)	TiO_2-SiO_2 heat treated for 2 h, at 600^0C	50	327	1.65
	A 2 (700)	TiO_2-SiO_2 heat treated for 2 h, at 700^0C	50	273	1.42
Sample A 3	A 3 (500)	TiO_2-SiO_2 heat treated for 2 h, at 500^0C	25	457	2.34
	A 3 (600)	TiO_2-SiO_2 heat treated for 2 h, at 600^0C	25	293	1.71
	A 3 (700)	TiO_2-SiO_2 heat treated for 2 h, at 700^0C	25	265	1.38

It can be observed (figure 1 a, b) that the A1 samples presents the highest peak, fact that indicates a greater local ordination degree. This could be explained by the present of the highest content of Ti (75%), which promotes the crystalline phase formation.

In figure 2 are presented the X-ray diffraction patterns realized with Cu radiation and Ni filter, of the A1 sample heat treated at 500^0, 600^0 and 700^0C. The X-ray diffraction patterns of the A1(500) sample is typical for an amorphous titania structure. The X-ray diffraction pattern of the A1 (600) sample presents a very large X-ray diffraction line at $2\theta = 25.30$ degree, typical for the most intense anatase (101) diffraction line, indicating the beginning of the crystallization of the anatase structure. This crystallization process is continued for the A1(700) sample but, at this temperature, a new TiO_2-SiO_2

crystallized system has been formed. The presence of a new TiO_2-SiO_2 crystallized system is indicated by the existence of a large X-ray diffraction maxima that is situated at $2\theta = 22.30$ degree in the diffraction pattern [15-19].

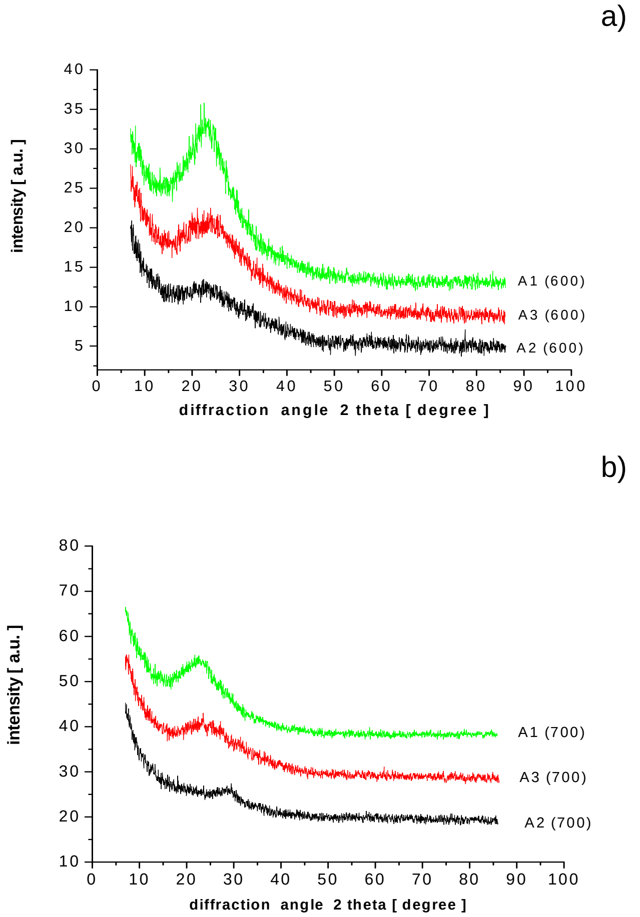

Figure 1. X-ray diffraction patterns of the TiO_2-SiO_2 aerogels heat treated at (a) 600^0C and (b) 700^0C, Co K_α (λCuK = 1.54178 Å) radiation, Fe filter.

The microstructural parameters of the A1 samples after heating at 600^0C and 700^0C showed an average size of D_{eff} = 25 Å for the TiO_2 nanocrystallites and a large value of the lattice microstrain $< \varepsilon^2 >^{1/2}$ (L) = 5÷6 × that suggests an important TiO_2 – Si intercrystallites interaction

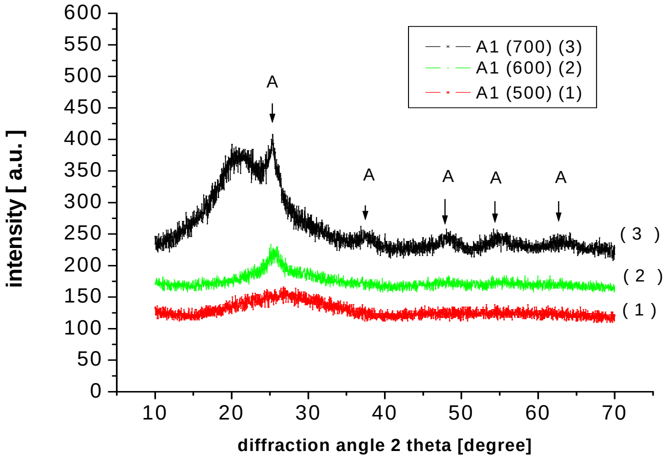

Figure 2. X-ray diffraction pattern for the samples A 1, heat treated at 500^0, 600^0 and 700^0C, Cu K_α .radiation, Ni filter.

The new TiO_2-SiO_2 crystallized system formed after heat treatment at 700^0C of the sample A1 has the lowest photocatalytic activity. In contrast, the salicylic acid decomposition rate constant of the A1(600) sample was for three times greater than for the A1(500) sample (Table 1), due to the anatase formed after heat treatment at 600^0C.

CONCLUSIONS

In this work, we prepared TiO_2-SiO_2 aerogels with different contents of Si, which are subsequently heat treated at different temperatures. The morpho-structure of the as obtained silica – titania aerogels was studied by X-ray diffraction and specific surface area measurements. The photocatalytic activity of the SiO_2-TiO_2 aerogels was determined by measuring the degradation rate of the salicylic acid used as reference organic material. The anatase phase is formed after heat treatment at 600^0C in case of A1 aerogels, which forms a new TiO_2-SiO_2 crystallized system after heat treatment at the 700^0C. This new crystallized system manifests low photocatalytic activity. The larger specific surface area has been determined for the sample A3 (500) with the higher Si content. The heat treatment performed at 600^0C and 700^0C allowed the formation of anatase phase, as well as the meso- to micropore transformation. The TiO_2-SiO_2 (1:1 molar ratio) aerogel, heat treated at 500^0C has the highest photocatalytic activity.

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