

Photocatalytic and structural properties of mixed titania and zirconia aerogels

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A series of $\text{TiO}_2\text{-ZrO}_2$ aerogels with different ZrO_2 contents (3-10 %) were prepared by an acid catalyzed sol-gel method followed by low-temperature supercritical drying and heat treatment. The structure and morphology of mixed aerogels were studied by means of Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), xenon sorption and elemental analysis. XRD spectra refinements show that the calcined $\text{TiO}_2\text{-ZrO}_2$ aerogels consist mainly in anatase phase accompanied by a small fraction of tetragonal ZrO_2 . The Raman spectra prove that the network of the calcined mixed aerogels mainly preserves an anatase structure similar to that of the calcined TiO_2 aerogel. The TEM images reveal that the anatase particles present round shapes with a highly homogeneous size (about 3-8 nm). Areas containing chains of amorphous tetragonal zirconia were also identified by the TEM investigations. The addition of zirconia to titania significantly increased the surface area and stabilized the anatase phase of titania. The best catalytic efficiency for the salicylic acid photodecomposition was obtained for the aerogel with 9.39 % zirconia that exhibited an apparent rate constant of about three times higher than that of the pure titania aerogel.

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1. Introduction

Morphological control of materials involves regulation of the overall outer structure, shape and size, as well as of the inner structure, pore size and connectivity, and, in the case of potential polymorphs, also of the crystal phase of the components. Novel inorganic networks with controlled morphology and properties can be fabricated using sol-gel or alco-thermal methods followed by supercritical drying [1-3]. Inorganic materials produced via these methods have advantages in applications where high porosities and a large specific surface, besides adsorption and surface mediated reactions, are key factors. Such an application is photocatalysis. Photochemical degradation can be used for the decomposition of toxic organic contaminants in wastewater [4]. This process involves the absorption of light by a semiconductor, forming electron and hole pairs, which can lead to oxidation and reduction reactions. Many organic and some inorganic compounds are degraded in aqueous dispersions of TiO_2 under illumination with UV light [5]. Synthesis of a TiO_2 material with ideal properties for a photocatalytic device requires a large surface area on which the heterogeneous surface catalysis reaction occurs, and enhanced porosity with rational pore connectivity to optimize the flow rate through the catalyst. Another means of improving the catalytic efficiency of metal oxides and their applicability as support materials for catalysis is the

doping of the metal oxide with a metal or to combine it with another metal oxide [6,7]. Examples of mixed oxides include the combination of TiO_2 with SiO_2 , ZrO_2 , or Al_2O_3 [8-13]. The combined metal oxide materials have new reactivity properties and higher activity when compared with the solitary metal oxide. A number of methods have been used to prepare mixed metal oxide materials including impregnation, selective grafting, chemical vapor deposition, mechanical mixing, coprecipitation, and solution sol-gel methods. The most important benefits of these processes lie in the homogeneity of the mixture of components and in the possibility to control the final metal-to-metal ratio. Combining the synthesis of binary metal oxide materials with the ability to maintain the structural properties of large porosity and large specific surface area should give improved catalytic efficiency due to the presence of a secondary metal oxide and to the possibility of a structural control.

Within this paper the formation of binary oxide (titania/zirconia) networks is accomplished by utilizing a sol-gel method followed by supercritical drying. The binary metal oxide materials are obtained by mixing the titanium and zirconium precursors followed by a series of hydrolysis and condensation reactions to form the networked structure of the gel. Our further interest was focused on analyzing the structure-performance relationship from a photocatalytic applications perspective. In order to evaluate the

photocatalytic efficiency of the mixed aerogels salicylic acid was used as a model compound. Salicylic acid chemisorbs to the titania surface via carboxylic groups [14-15] and has spectral characteristics allowing the simple study of its decomposition.

2. Experimental

2.1 Sol-gel-aerogel preparation

The sol-gel process was carried out at ambient temperature under normal atmosphere. Two different solutions were prepared. A first solution contained 6.75 ml tetra-iso-propyl ortotitanate - TIP (Merck; > 98%) in 10 ml ethanol and a second one 0.3-1.2g zirconium acetylacetonate (Merck, > 98%), doubly distilled water and nitric acid in 10 ml ethanol. After homogenizing both solutions for several minutes the first solution was quickly added to the second under vigorous stirring. The corresponding molar ratios are presented in Table 1.

Table 1. ZrO_2 content, specific surface area (S_{BET}) and apparent rate constant for the ZrO_2 - TiO_2 aerogels obtained in different molar ratios of the reactants, calcined at 773 K for 2h.

Sample $\text{TiO}_2/\text{ZrO}_2$	TIP:EtOH:H ₂ O:H NO ₃ :AcAcZr Molar ratios	ZrO ₂ [%]	S_{BET} [m ² /g]	$10^3 \times$ k_{app} [min ⁻¹]
11.4/1	1:14.91:6.26:0.007 1:0.089	9.39	230	9.6
18.3/1	1:14.91:4.21:0.007 1:0.054	6.12	190	8.2
37/1	1:14.91:2.39:0.007 1:0.026	3.17	174	7.4

The resulted mixture was stirred until a gel formed. The gels were covered and allowed to age for six months at room temperature. The alcohol was then removed by supercritical drying with liquid CO₂ using a SAMDRI - PVT -3D dryer (Tousimis Res. Corp. USA). The primary aerogels were calcined at 773 K for 2h in the air using a CARBOLITE furnace and characterized.

2.2 Photocatalytic activity

The salicylic acid was used as a model compound to study photodegradation on TiO_2 - ZrO_2 aerogels. Stock solution of 10 mM salicylic acid and a salt solution of 1.1 mM KCl at pH 3.7 were prepared and used for all experiments. In each experiment, 6 ml of the salicylic acid was added in a cell to 0.1 g aerogel. As initial ratio between salicylic acid and TiO_2 - ZrO_2 30 μmoles salicylic acid per 1 g aerogel was chosen. The cell was kept 30 min in the dark before the degradation experiment. The photodegradation profile was obtained from measuring the concentration of salicylic acid with a Jasco V-530 spectrophotometer (from the decrease in intensity of the electronic absorption band of salicylic acid located at 295 nm). Photodecomposition

experiments were performed in a Teflon cell with a quartz window for UV illumination using a 250 W high pressure Hg lamp. The irradiation intensity determined by a Eppley PSP Radiometer was 8 W/m². The photodecomposition reaction follows a pseudo-first order kinetics, and hence the apparent rate constant was calculated by plotting $\ln(C_0/C)$ vs time. The slope of the plot after applying a linear fit represents the apparent rate constant [16].

2.3 Characterization

Elemental analysis was performed with an inductively coupled plasma-mass spectroscopy (ICP-MS).

The BET surface areas (S_{BET}) was derived from krypton physisorption measurements at 77 K using a home-made glass installation. Prior to measurements, the samples were degassed to 0.001 Pa at 448 K. S_{BET} was calculated in the relative pressure range of 0.05-0.35, assuming a cross-sectional area of 0.195 nm² for the krypton molecule.

The Raman measurements of the investigated aerogel samples were performed on a Horiba/Jobin-Yvon Labram system equipped with a Leica PL FLUOTAR X100/0.75 microscope objective, a 1800 lines/mm grating and a frequency doubled Nd:YAG laser with an emission wavelength of 532 nm. For recording the micro-Raman spectra a power of 20 mW incident on the sample was employed. The spectral resolution used for all measurements was smaller than 1 cm⁻¹.

The structure of the powders was examined using a DRON X-ray powder diffractometer linked to a data acquisition and processing facility. $\text{CuK}\alpha$ radiation ($\lambda = 0.1540598$ nm) and a graphite monochromator were used.

A JEOL 200 CX TEM operating at an accelerating voltage of 200 kV was employed to obtain bright (BF) and dark (DF) field images as well as the electron diffraction patterns of the mixed oxide nanoparticle system. Particle sizes were measured from BF and DF images whereas the phase content was investigated by using electron diffraction patterns. Samples were prepared by dipping a 3 mm holey carbon grid into ultrasonic dispersed oxide powder in ethanol.

3. Results and discussion

The surface areas of the mixed $\text{TiO}_2/\text{ZrO}_2$ vary from 174 to 230 m² g⁻¹ for an increasing ZrO_2 amount, as presented in Table 1. One can also observe that the rate constants determined via salicylic acid photodegradation in the presence of the ZrO_2 - TiO_2 aerogels increase for an increasing zirconia content (see Table1). It is known that zirconia has a very large band gap, greater than 5 eV and therefore it cannot act as a photocatalyst for the applied irradiation conditions. However, zirconia is a good adsorbent [17]. On the other hand, it is generally accepted that the TiO_2 - anatase is photocatalytically more active than its rutile phase [18] and the addition of up to 10% of zirconia to titania inhibits the anatase-to-rutile phase transformation [13, 19]. In addition, salicylic acid forms a

complex with the surface of the anatase crystal, which facilitates the hole transfer [14, 15]. Taking into consideration all these facts the better photocatalytic activity of the investigated $\text{TiO}_2/\text{ZrO}_2$ aerogels in comparison to that of the pure TiO_2 aerogels ($k_{\text{app}} = 3.5 \times 10^{-3} \text{ min}^{-1}$) can be explained.

Fig. 1 shows the Raman spectra recorded for the heat-treated aerogels. Well-defined Raman bands around 144, 197, 399, 517 and 639 cm^{-1} due to the TiO_2 anatase crystalline phase are observed. Considering the convolution of two fundamental peaks near 517 cm^{-1} , these six peaks correspond to the well-known six fundamental vibrational modes of anatase TiO_2 transforming like E_g , E_g , B_{1g} , A_{1g} , B_{1g} and E_g , respectively [20-23]. A close analysis of the spectra reveals the presence of other three very weak Raman bands around 245, 320 and 365 cm^{-1} , especially for the aerogel sample exhibiting a smaller ZrO_2 content. Such spectral features were previously observed, when ultrafine TiO_2 powders with grain sizes around 10 nm were investigated, and were attributed to the existence of a little amount of brookite [21, 24, 25].

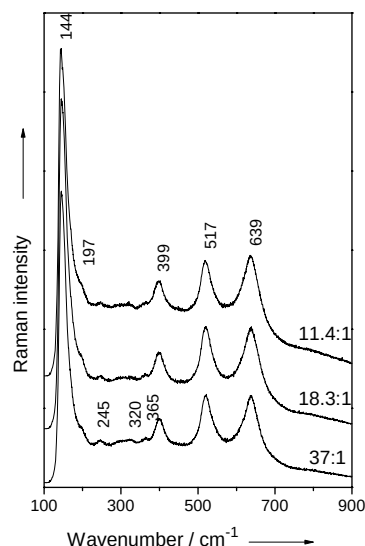


Fig. 1. Raman spectra of some $\text{TiO}_2/\text{ZrO}_2$ aerogels having different Zr contents and calcined at 773 K for 2 hours.

Spectral characteristics that can be directly assigned to a crystalline phase of ZrO_2 have not been evidenced in the Raman spectra, though a slight broadening of the most intense bands (144, 399, 517 and 639 cm^{-1}), but mainly of the 144 cm^{-1} band (from 17.3 to 19.6 cm^{-1}) was observed for an increasing Zr content. This broadening is most probably due to the presence of a tetragonal phase of ZrO_2 , which gives medium and intense bands at 145 cm^{-1} (E_g), 265 cm^{-1} (A_{1g}), 322 cm^{-1} (B_{1g}), 466 cm^{-1} (E_g), 609 cm^{-1} (B_{1g}) and 642 cm^{-1} (E_g). A precise assessment of these spectral changes becomes very difficult since the Raman bands of ZrO_2 and TiO_2 appear in the same spectral regions, however it can be inferred that the network of the calcined mixed aerogels mainly preserves the anatase structure similar to the heat-treated TiO_2 aerogel. The substitution of a part of the Ti atoms with Zr atoms during the preparation and

consequently the existence of Ti-O-Zr bonds after thermal treatment is also feasible.

The X-ray diffraction measurements show that the calcined $\text{TiO}_2/\text{ZrO}_2$ aerogels contain as major phase anatase and a small fraction (between 0.5-1%) of cubic or tetragonal ZrO_2 (Fig.2).

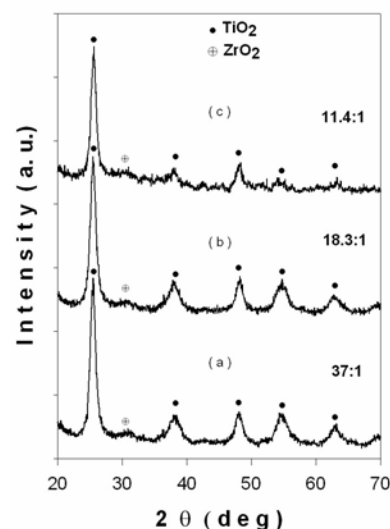


Fig. 2. X-ray diffraction patterns of some $\text{TiO}_2/\text{ZrO}_2$ aerogels having different Zr content and calcined at 773 K, 2h.

For the sample with the lowest Zr content (Fig. 3), a mean anatase particle size of 5 nm and a uniform porosity with $r = 8-10$ nm, typical for samples with a low ZrO_2 content, were found.

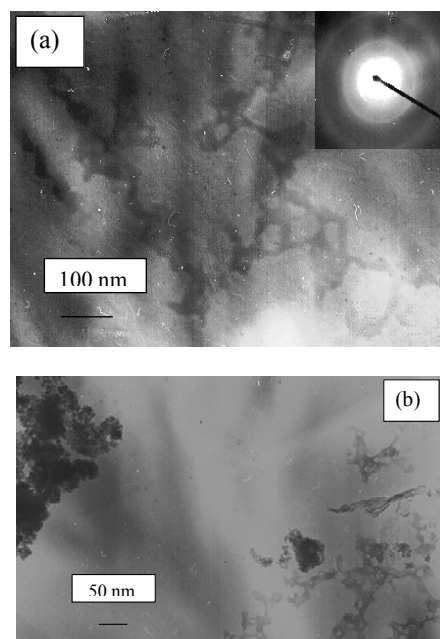


Fig. 3. TEM images in the specimen having $\text{TiO}_2/\text{ZrO}_2=37:1$ and thermally treated at 773 K, 2h: a) an area containing chains of amorphous tetragonal zirconia; b) other area containing the both types of structures (anatase and zirconia particles).

However, an important fraction of amorphous material is present (Fig. 3a) organized in long and extended chains having thicknesses of 10–20 nm, with a weak contrast and exhibiting a SAED pattern with extremely broadened diffraction rings. The position of the strongest rings is placed at $d = 3.00 \text{ \AA}$ and $d = 1.85 \text{ \AA}$ which are close to the main lines of the tetragonal modification of zirconia. In many areas, the anatase particles and amorphous chains can coexist (Fig. 3b). The addition of zirconia stabilizes the TiO_2 anatase form, since the rutile phase could not be detected [13]. However, a zirconia content inhibits crystallization, as a weak crystallinity could be detected by X-ray measurements in this specimen. For the sample having a medium content of Zr, only the anatase particles are present (Fig. 4a) and a pure anatase phase can be identified (Fig. 4b) which suggests a possible substitution of Ti atoms with Zr atoms [25], indicating thus a homogeneous mixing of the Ti and Zr components.

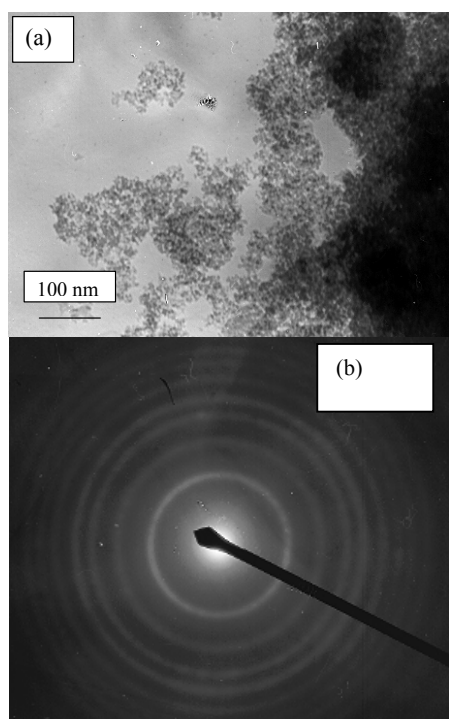


Fig. 4. TEM image (a) and SAED pattern (b) of anatase nanoparticles in the specimen having $\text{TiO}_2/\text{ZrO}_2=18.3:1$ and thermally treated at 773 K, 2h.

Fig. 5 shows a TEM image and SAED pattern of anatase nanoparticles having a maximum content of ZrO_2 and thermally treated at 773 K for 2h. The mean size of crystallites is slightly bigger but a high agglomeration rate is registered. A coexistence of anatase particles and amorphous chains of tetragonal zirconia is observed also in this specimen (Fig. 6a) but the mean chain thickness increased (Fig. 6b) as compared to the first specimen.

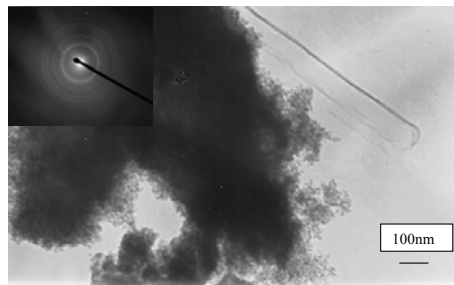


Fig. 5. TEM image and SAED pattern of anatase nanoparticles in the specimen having $\text{TiO}_2/\text{ZrO}_2=11.4:1$ and thermally treated at 773 K, 2h.

The pore size and their connectivity increases as compared to the specimen with the minimal Zr content. This result is in good agreement with the data obtained from the BET investigations. A close analysis of the results derived from TEM pictures elucidates an already discussed Raman spectral feature.

It is now clear that the slight broadening of the Raman band observed, as the Zr content increases, originates from the presence of the amorphous tetragonal zirconia.

We have found, according to previous results [27], that the average pore diameter shifts slightly towards higher values, and the pore volume becomes lower, when ZrO_2 is incorporated into the titanium oxide.

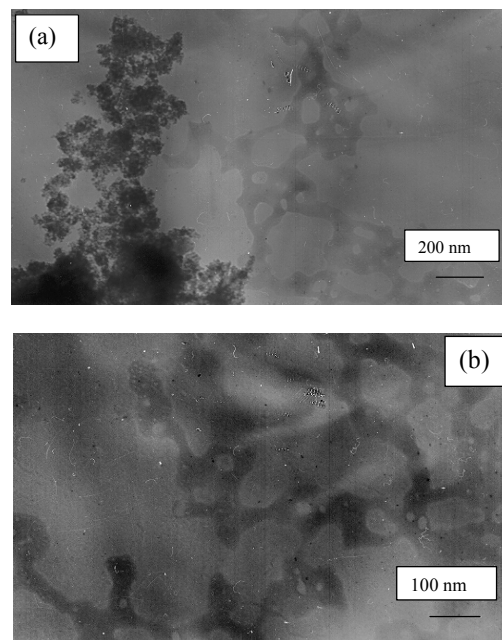


Fig. 6. TEM images in the specimen having $\text{TiO}_2/\text{ZrO}_2=11.4:1$ and thermally treated at 773 K, 2h: a) an area containing the both types of structures (anatase and zirconia particles); b) other area containing chains of amorphous tetragonal zirconia.

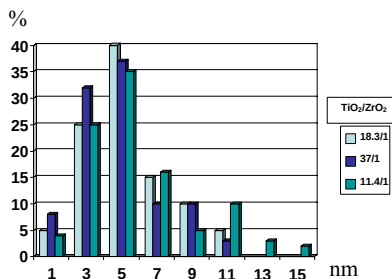


Fig. 7. Histogram of anatase particle sizes in the aerogels of $\text{TiO}_2\text{-ZrO}_2$.

The histogram of size distribution of anatase particles (Fig. 7) shows a little increase of the mean size as the Zr content increases and also, for maximum Zr content, a distribution tail to higher sizes was found.

All samples present round shapes of small aggregated subparticles with a highly homogeneous size (about 3-8 nm).

5. Conclusions

$\text{TiO}_2\text{-ZrO}_2$ aerogels with different ZrO_2 contents (3-10 at %) have been prepared by an acid catalyzed sol-gel method followed by low-temperature supercritical drying. XRD, TEM and Raman investigations revealed the structural and morphological peculiarities of the $\text{TiO}_2\text{-ZrO}_2$ aerogels. The system consists of a dominating TiO_2 anatase phase accompanied by a small amount of tetragonal ZrO_2 . The particle dimension of the anatase phase was found to be in the range of 3-8 nm. TEM images revealed the presence of amorphous zirconia. It was shown that the addition of zirconia to the titania significantly increases the surface area and stabilizes the anatase phase of titania. It was also established that the catalytic performances of the aerogels are improved when adding zirconia. The best catalytic efficiency of $\text{TiO}_2\text{-ZrO}_2$ aerogels was obtained for the maximum content of zirconia (9.39 %) that exhibited an apparent rate constant of about three times higher than that of the pure titania aerogel. This behavior was attributed to the increased surface area, to the presence of anatase phase of the titania as well as to the adsorptive properties of zirconia, which is believed to increase the local concentration of the reactant near the catalyst surface. Binary metal oxide materials synthesis by sol-gel method followed by low-temperature supercritical drying can lead to interesting catalysts with improved catalytic performances.

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