

High loading TiO₂ and ZrO₂ nanocrystals ensembles inside the mesopores of SBA-15: preparation, texture and stability

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Abstract

TiO₂ (30–80 wt.%) and ZrO₂ (48–75 wt.%) were inserted inside the pores of SBA-15 mesostructured silica host by chemical solution decomposition (CSD) or internal hydrolysis (IH) of the corresponding alkoxides. Both methods yielded composites with 85–94% TiO₂ crystallinity (anatase). In case of ZrO₂, CSD yielded >95% crystallinity (tetragonal phase), while IH gave an amorphous ZrO_x-phase that does not crystallize up to 1073 K. The guest Ti(Zr)-oxide phases did not block the SBA-15 pores, and their surface was fully accessible for nitrogen adsorption. Calcination in air of TiO₂/SBA-15 and ZrO₂/SBA-15 (CSD) composites up to 1073 K did not change the nanocrystals structure and slightly increased the domain size derived from XRD data from 5.0–8.5 to 6–10 nm for TiO₂ (IH and CSD) and from 4.5 to 6.5 nm for ZrO₂ (CSD). After the same treatment the crystals domain size of bulk reference TiO₂ increased to >100 nm with full conversion to rutile polymorph and of reference bulk ZrO₂—to 20–25 nm with partial conversion to monoclinic modification. Thorough characterization of the texture, structure, location and dispersion by HRTEM, SAXS, EDS, SEM, XRD, N₂-adsorption methods allowed evaluation of the assembling mode of TiO₂ and ZrO₂ inside SBA-15 nanotubes: amorphous layer, ensemble of small 4–5 nm crystals (TiO₂-IH and ZrO₂-CSD) or single large 8.5 nm crystals (TiO₂-CSD).

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1. Introduction

Ordered mesostructured silicas (OMS) with adjustable pore size and close to maximal possible specific surface area [1,2] provide wide opportunities for synthesis of advanced materials with different functionalities serving as catalysts, chemical sensors, materials with wholesome optical and magnetic properties [3–5]. Various guest phases (GP) such as metals, pure and mixed metal

oxides, sulfides, heteropoly-compounds and others could serve as “functionalization source” being assembled in the pore system of OMS as nanoparticles with distinct structure. The unique pore geometry and high surface area of OMS hosts allows substantially higher loading of GP relative to the traditional porous supports like silica-gel or activated alumina—up to 70 wt.% even filling only 50% of the pore volume (Table 1). The properties of embedded GP/OMS composite materials are determined, besides GP loading, by location of GP nanoparticles ensemble inside the hosts pore system, the particles assembling mode with minimal pores blocking and by the crystallinity of target GP. Yet the simultaneous control of all these parameters is a very complicated practical problem. Thus only few examples of successful preparations of GP/OMS materials were

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Table 1
Calculated possible guest phase loadings into SBA-15 material

Catalytic phase	Filling of pore volume in SBA-15 (vol%)	Guest phase loading y^a (wt.%)
ZrO ₂	100	85
	50	74
TiO ₂	100	80
	50	67

^a For 100% filling $y = \rho/(1 + \rho) * 100\%$, for 50% filling $y = \rho/(2 + \rho) * 100\%$, where ρ —theoretical density of crystals (3.9 g/cm³ for TiO₂ and 5.8 g/cm³ for ZrO₂). Pore volume of parent SBA-15 was taken equal to 1 cm³/g.

reported that substantially excel in performance the corresponding GP embedded in traditional matrixes or the bulk GP materials. Among them, preparation of catalytic materials by insertion the Fe₂O₃ in MCM-41 [6], WS₂ [7], SO₄-ZrO₂ [8], Pt-TiO₂ [9] and phosphorotungstic heteropolyacid [10] in SBA-15 matrixes were reported. Silicon clusters [11] and CdS nanoparticles [12] in oriented OMS films demonstrated unique photoluminescence performance. Super magnetic behavior of iron nanoparticles inside the OMS matrix was detected in [13].

The crystalline titania is widely used as a basis for oxidation [14], selective catalytic reduction [15] and photo catalysts [16]. Stabilized TiO₂ nanocrystals are used as efficient gas sensors [17] and high performance photovoltaics [18]. Tetragonal zirconia modified with sulfate anions forms a highly acidic catalytic phase with an excellent performance in a variety of acid-catalyzed reactions [19,20]. Zirconia-based air-fuel ratio sensors are widely used for automotive applications [21]. For the most of these purposes, especially in catalytic applications, the performance of crystalline phases exceed by far those of amorphous phases [14,15,19,20]. Furthermore, application of nanocrystals with high surface area yields better performance. However, due to high sintering ability it is very difficult to prepare TiO₂ and ZrO₂ phases as thermally stable nanocrystals with high surface area [22]. Therefore stabilizing them as GP inside the OMS matrixes received much attention in the last years. It is reflected by tens of publications related to TiO₂/OMS [23–35] and ZrO₂/OMS [36–52] composites.

Ti-oxide phase was inserted into MCM-41 [23,24], MCM-48 [34], SBA-15 [23,25–30] and metal (V, Cr, Fe)-substituted MCM-41 [33]. Commonly Ti-alkoxides were used as Ti-phase precursor and they were inserted directly together with the silica source during OMS synthesis [28] or by postsynthetic modification of OMS via grafting [29,32,34,35] or impregnation followed by solvent evaporation [24,27,30,31,33] or Ti-precursor hydrolysis [23]. However, all the TiO₂/OMS samples prepared by postsynthetic grafting or by direct insertion during OMS synthesis did not contain crystalline TiO₂ due to isomorphous substitution of surface silicon atoms by

titanium leading to location of Ti in the silica framework inside the OMS pore walls, or formation of isolated grafted Ti-species [25,26,28,29,32,34,35]. For the similar reasons, impregnation did not lead to formation of crystalline TiO₂ phase at low loadings of Ti-phase (<10 wt.% of TiO₂) [24,27,30]. Thus, crystalline TiO₂ was obtained in TiO₂/OMS composite materials only at high loadings >20 wt.% [23,24,30,31,33]. The information about the size, dispersion, location and assembling mode of the TiO₂ nanocrystals inside OMS in these works is limited and sometimes contradictory. TiO₂-anatase film formation was claimed in [30] based on the results of spectroscopic methods and shift of pore diameter to the lower values. Though no crystal domain size (XRD) or particles size (TEM) was provided in [30], the sharp peaks in XRD patterns of high loading 21–57 wt.% TiO₂/OMS materials seems to contradict with the TiO₂-film formation hypothesis, while shift of pore diameter to the lower values may occur also after insertion of nanocrystals. Significantly different TiO₂ crystal sizes were obtained in [31] from XRD (18–20 nm) and TEM (5 nm) measurements of TiO₂/OMS composites with Si/Ti = 2.5–10 suggesting that at least part of TiO₂ crystals with diameter exceeding the OMS pore size were located outside the OMS pores. The crystal domain size of 5–10 nm measured in [23,24] for 20–60 wt.% TiO₂/SBA-15 (or MCM-41) composites by XRD correlated well with TEM data. However, no data were provided on the content of crystalline TiO₂ phase relative to the total Ti loading. This information is very important since the significant part of Ti-phase may substitute silicon atoms in the silica framework as was mentioned above. Small shift of pore size distribution to lower pore diameters obtained for 60 wt.% TiO₂/SBA-15 material in [23] suggests that significant part of Ti may substitute the silicon in OMS walls. In addition, the possible pore blocking effect was not clarified both in [23,24].

The Zr-oxide phase was inserted into OMS commonly as sulfated zirconia [39,41–46,50,51] or gallium [47,48] and alumina [49] promoted sulfated zirconia. Insertion of pure ZrO₂ was reported as well [36–38,40,52]. Addition of Zr-source together with the silica source during the MCM-41 synthesis did not yield crystalline Zr-oxide phase due to location of Zr atoms in the silica framework inside the pore walls [36,37]. XRD-amorphous zirconia/OMS composites were obtained at low loadings of 10–26 wt.% ZrO₂ by postsynthetic modification of OMS [40,44,45,51,52]. Some of amorphous Zr-oxide phase exists in such composites as small (2–3 nm) zirconia particles which were visualized by bright-field electron tomography [38]. Increasing the ZrO₂ loading beyond 10 wt.% [44] or 22–26 wt.% [51,52] resulted in formation of crystalline ZrO₂ phase detected by XRD, while amorphous Zr-oxide phase was obtained via grafting of Zr(OPr)₄ on the OMS pore walls at 50 wt.% ZrO₂ loading [46]. No information

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