Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Microporous composite SiO_2-TiO_2 spheres prepared via the peroxo route: Lead(II) removal in aqueous media

Roman Morozov[a], Igor Krivtsov[a,b,*], Viacheslav Avdin[a], Zakariae Amghouz[c], Alexander Gorshkov[a], Ekaterina Pushkova[a], Oleg Bol'shakov[a], Aleksandra Bulanova[a], Marina Ilkaeva[d]

[a] *Department of Chemistry, South Ural State University, 454080 Chelyabinsk, Russia*
[b] *Department of Physical and Analytical Chemistry, University of Oviedo-CINN, 33006 Oviedo, Spain*
[c] *Department of Materials Science and Metallurgical Engineering, University of Oviedo, Campus Universitario, 33203 Gijón, Spain*
[d] *Department of Organic and Inorganic Chemistry, University of Oviedo-CINN, 33006 Oviedo, Spain*

ARTICLE INFO

Keywords:
SiO_2
TiO_2
Spherical particles
Silica-titania
Microporous
Lead adsorption
Peroxo method

ABSTRACT

Composite microporous SiO_2-TiO_2 spheres and micro/mesoporous TiO_2 spheres were prepared via the template-free two-step synthetic route using aqueous peroxotitanate solution and tetraethyl orthosilicate (TEOS) as precursors. Both the composite SiO_2-TiO_2 and pure TiO_2 spheres prepared by the solvent-exchange method were initially non-porous, but the applied reflux treatment in water-ethanol suspension successfully transformed them into microporous materials with high apparent surface areas approaching 500 $m^2 \cdot g^{-1}$ and the micropore volume of 0.17 $cm^3 \cdot g^{-1}$, while maintaining the same morphology. The prepared composites retained high values of pore volume and specific surface area up to 400 °C of thermal treatment temperature. The crystallization of TiO_2 into the anatase phase in the mixed oxide occurred only at 700 °C, that process was also accompanied by the significant reduction of pore volume, as well as apparent surface area values. The prepared materials were tested as adsorbents for the lead(II) removal; they demonstrated high adsorption capacities, reaching 340 $mg(Pb^{2+}) \cdot g^{-1}$. Moreover, the mixed silica-titania oxide was found to be more efficient adsorbent at low pH values.

1. Introduction

Silica- and titania-based functional materials are frequently used for various environmental applications due to their high chemical stability, non-toxicity and low cost. It is a common notion that the formation of silica-titania composites might significantly modify and improve some properties of the constituents, widening the application range of these materials [1–10]. This occurs because of the Si—O—Ti linkages formation in the bulk and on the surface of the mixed oxide, creation of tetracoordinated titanium fragments, and stabilization of titania in an amorphous state. The acidity arising from the above mentioned structural changes makes SiO_2-TiO_2 an interesting active material for various catalytic processes [1–3,10–12]. However, the preparation of a molecularly homogeneous silica-titania composite via sol-gel or precipitation routes meets with obstacles. Titanium has significantly larger partial positive charge than silicon, which makes it very reactive in the presence of water, thus tending to form hydrous titania. Thus, certain measures preventing the separation of the two oxides implying the use of anhydrous organic solvents [13], complexing agents [14], or prehydrolysis of the less reactive silica precursor [15] are commonly applied. Obviously, the control of hydrolysis and condensation rates of titanium oxo-hydroxo complexes and their interaction with silica species is even more complicated in aqueous medium. The means of manipulating TiO_2 precursors hydrolysis rates and molecular homogeneity in water-born systems generally include the use of carboxylic acids [16] and amines [17] as complexing agents.

Other important aspects of silica-titania properties determining the performance in catalytic reactions and as catalytic supports are morphology, specific surface area (SSA), and porous structure. Spherical morphology is a very convenient form of the particles used as catalysts and adsorbents because it provides dense and uniform packing and favors establishing a laminar flow in such processes as catalysis [1–3], gases separation [4–7], and adsorption [18–21]. Though the methods for spherical SiO_2 fabrication via the Stöber process [22] and for TiO_2 using inorganic and structure-directed routes [23] are well-known, the reports on the preparation of silica-titania spheres with a high degree of the SiO_2 and TiO_2 mutual mixing are scarce. The porous structure of such composites is a key feature for many applications. Microporosity

---

* Corresponding author at: Department of Physical and Analytical Chemistry, University of Oviedo-CINN, 33006 Oviedo, Spain.
E-mail address: krivtsovigor@uniovi.es (I. Krivtsov).

https://doi.org/10.1016/j.jnoncrysol.2017.11.031
Received 18 September 2017; Received in revised form 14 November 2017; Accepted 17 November 2017

Please cite this article as: Morozov, R., Journal of Non-Crystalline Solids (2017), https://doi.org/10.1016/j.jnoncrysol.2017.11.031

provides accessibility for small molecules and ions to the active sites of silica, titania and mixed silica-titania materials making them useful in membrane separation technologies [4–7,24] and cation exchange [25,26].

The possibility of application of inorganic materials for adsorption of toxic metal cations from water by adsorption and ion exchange attracts significant interest. Among the variety of heavy metal pollutants found in waste and drinking water, the presence of lead is especially worrying. Water-soluble lead(II) acetate and volatile tetraethyl lead, often encountered in industry, are extremely harmful to humans and environment. Microporous TiO_2 and SiO_2-TiO_2 metal oxides demonstrate equal or higher efficiency in lead uptake from water solutions than the widespread organic polymeric resins [27] or carbon-based adsorbents [28], moreover, their superior chemical and thermal stability make them more promising for long-term application.

Earlier, we described the template-free preparation of homogeneous silica-titania spherical particles with controlled particle sizes [29]. However, low SSA and non-porous nature made their use impossible in many processes. Here, we report the surface activation procedure able to convert non-porous silica-titania spheres into highly microporous solids. Moreover, in this study we address the possible application of both titania and silica-titania materials for Pb^{2+} removal.

2. Experimental

2.1. Chemicals

Titanium oxysulfate hydrate ($TiOSO_4 \cdot H_2O$) containing 17% of H_2SO_4 used as titania source was provided by Alfa Aesar. TEOS (tetraethyl orthosilicate) of analytical grade produced by Reachim was used as the precursor for silica. Aqueous ammonia ($NH_3 \cdot H_2O$) solution of 25 wt%, HCl(aq), *n*-propanol, H_2O_2, $(CH_3COO)_2Pb$ (analytical grade), 2,7-bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III), acetic acid, and CH_3COONa were of analytical grade and were also produced by Reachim.

2.2. Synthesis of nonporous silica-titania spheres

Preparation of the composite SiO_2-TiO_2 spheres was performed according to the peroxo-mediated solvent exchange route reported in [29,30]. For the synthesis, 2.4 g of titanium oxysulfate (containing 10 mmol of TiO_2) was dissolved in 20–30 mL of deionized water at room temperature and immediately 10 mL of ammonia solution was added to it leading to the formation of white colloidal precipitate. The suspension was thoroughly mixed to ensure complete precipitation of hydrous titania, centrifuged and washed 6 times with deionized water, in order to remove sulfate and ammonium ions. The washed precipitate was placed in an ice bath and 10 mL of H_2O_2 was dropwise added to it, while the suspension was vigorously stirred. Eventually, the complete dissolution of the colloidal precipitate occurred and a transparent yellow solution of titanium peroxo complex was formed. The volume of the titanium peroxo complex solution was adjusted to 100 mL with deionized water and its pH was set to 9.5 by ammonia addition.

Separately, 2.2 mL of TEOS was dissolved in 97.8 mL of *n*-propanol. The choice of the solvent was based on the previous work [29]. The solution of TEOS in *n*-propanol was magnetically stirred for a few minutes and then poured into the aqueous titanium peroxo complex. The mixture turned turbid instantaneously and was left stirring for 24 h. Subsequently, the suspension was centrifuged, washed 6 times with deionized water and dried under vacuum at 50 °C for 6 h.

For the preparation of pure TiO_2 no TEOS solution was used, instead 100 mL of *n*-propanol was directly poured into the peroxotitanate water solution while magnetically stirred, after 24 h of mixing, the precipitate was washed and dried according to the procedure described in [31].

Pure SiO_2 was synthesized following the same protocol, but in the absence of TiO_2 source.

2.3. Surface area activation of the prepared spheres

The silica-titania spherical particles prepared via the method described above were nonporous [29]. In order to modify their porous characteristics, the surface area activation procedure reported earlier for pure TiO_2 spherical particles [31] was implemented. The activation was performed by a post-synthetic treatment in the following way: freshly prepared nonporous silica-titania spheres were suspended in 50 mL of water-ethanol mixture (1:1 ratio by volume) at the pH value of 5, which was set by addition of HCl (1 M). The suspension was refluxed for 21 h and then the solid phase was separated by centrifugation at 3000 rpm, washed with deionized water and dried at 50 °C for 24 h. The silica-titania samples prepared in this way were designated as ST50, the same materials calcined at 400 °C and 700 °C in air for 1 h were marked ST400 and ST700, respectively. The titania spheres prepared using the same procedure were designated as T50, T400, and T700 depending on the calcination conditions they underwent. The procedure of surface area activation of pure SiO_2 was similar to that applied for the TiO_2 and the composite SiO_2-TiO_2 samples.

2.4. Characterization

Morphological investigation of the prepared composite silica-titania spheres was performed by a field emission scanning electron microscope (SEM) JEOL JSM 7001F. The SSA, volume and size distribution of micro- and mesopores were probed by N_2 adsorption at 77 K using an ASAP 2020 Micromeritics analyzer. The as-prepared samples were outgassed at 100 °C for 2 h, while the samples calcined at 400 °C and 700 °C were outgassed for 2 h at 300 °C. The XRD patterns were recorded on a Rigaku Ultima IV diffractometer operating at Cu Kα radiation ($\lambda = 0.154$ nm). The mean size of anatase crystals was calculated by Scherrer equation for (101) reflection of anatase phase. Thermoanalytical studies were performed using a simultaneous TG-DSC thermal analyzer Netzsch 449 F1 in the temperature range from 25 to 1000 °C in air flow at the heating rate of $10\ ^{\circ}C \cdot min^{-1}$. A Jeol JEM-2100F transmission electron microscope (TEM) equipped with a field emission gun (FEG) was applied for TEM observations. Sample preparation involved dispersion in ethanol, sonication and deposition on a holey carbon film-coated copper grid with subsequent drying, a Gatan SOLARUS 950 was used before investigation. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a SPECS system equipped with a Hemispherical Phoibos analyzer operating at Mg-Kα radiation ($h \cdot \upsilon = 1253.6$ eV). The FTIR spectra were collected using a Shimadzu IR Affinity spectrometer. The point of zero charge (PZC) of pure titania and silica-titania spheres was measured by a Zetasizer Nano ZS90.

2.5. Lead adsorption experiment

Adsorption of Pb^{2+} ions was studied under isothermal conditions at 25 °C. Kinetic study of Pb^{2+} ion adsorption was carried out in the following way: to 50 mL of the 500 $mg(Pb^{2+}) \cdot L^{-1}$ solution of lead(II) acetate 20 mg of adsorbent was added and the suspension was left shaking. The probes were withdrawn at fixed time intervals and the concentration of lead ions was measured photometrically.

For adsorption isotherm measurement, 25 mL of lead(II) acetate solutions with concentrations of 10, 25, 50, 100, 150, 200, 300, 400 and 500 $mg(Pb^{2+}) \cdot L^{-1}$ were placed into glass beakers containing 10 mg of adsorbent and shaken for 1 h. No buffer solution was added and the pH value of the resulted suspensions was found to be equal to 5. In a separate experiment, intending to establish the effect of pH on adsorption capacity, diluted HNO_3 was added to the suspension of lead acetate solution and adsorbent and pH values were set to 1, 2, 3, and 4. After 1 h of shaking, the suspension was centrifuged and Pb^{2+} concentration was measured.

The concentration of Pb^{2+} ions was determined by the photometric