



Titania–silica–phosphonate triconstituent hybrid mesoporous materials as adsorbents in gas and liquid phases

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ARTICLE INFO

Article history:

Received 27 July 2010

Received in revised form 7 November 2010

Accepted 22 November 2010

Keywords:

Titania–silica–phosphonate

Mesoporous

Adsorbents

Metal ion adsorption

ABSTRACT

Mesoporous titania–silica–phosphonate (TSP) hybrid materials with different Si/Ti molar ratios have been synthesized by triconstituent assembly through oil-in-water microemulsion strategy with the use of Si(OEt)₄, TiCl₄ and sodium salt of ethylene diamine tetra(methylene phosphonic acid) as Si, Ti and P sources, respectively, and cetyltrimethylammonium bromide as surfactant template. The integration of silica into titania–phosphonate hybrids resulted in the improvement of regularity of mesoporous structure and the enlargement of surface area and pore volume of the hybrid materials, confirmed by low-angle powder X-ray diffraction, transmission electron microscopy and nitrogen adsorption–desorption analysis. The synthesized TSP triconstituent hybrid mesoporous materials have a preferable BET surface area up to 670 m²/g with large pore volume of 1.1 cm³/g. And the adsorption measurements of the synthesized TSP materials for CO₂ in gas phase and Cd(II) ions in liquid phase were tested, indicating their potential applications as multifunctional adsorbents for environmental protection.

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1. Introduction

Hybrid mesoporous materials that combined inorganic and organic moieties have attracted great attention because of their potential for integrating the physical and chemical properties of different components [1,2]. Metal/oxide organophosphonate-based compounds, as an important family of the organic–inorganic hybrid materials, have been widely studied owing to their potential applications in catalysis, ionic exchange and molecular separation [3–8]. The recently reported porous titania–phosphonate hybrid materials by using sodium salts of ethylene diamine tetra(methylene phosphonic acid) (EDTMPS) and diethylene triamine penta(methylene phosphonic acid) (DTPMPS) as coupling phosphorus molecules exhibited high photocatalytic activity in photodecomposition of Rhodamine B dye molecules and a large capacity for selective adsorption of Cd (II) ions [9]. However, the pore structures of these hybrid materials obtained by sol–gel method were quite poor with low specific surface area (159 m²/g) and small pore volume (0.32 cm³/g), and no information from low-angle X-ray diffraction was provided though their pore size distributions were in the mesopore range. Thus it is necessary to find a facile route to improve structural and textural properties of these hybrid materials for multifunctionality and practical applications.

Surfactant-templating strategy has been utilized for the mesoporous materials of various compositions with high surface areas and narrow pore size distributions [10,11]. Ordered mesoporous aluminum [12–14] and titanium [15] phosphonates with different organic groups bridged inside the frameworks were reported by either cationic or nonionic surfactant templating. The presence of surfactant in the self-formation of hierarchical meso-/macroporous materials was found to efficiently improve their porosity and textural property [16,17]. High-surface-area porous titanium phosphonate materials have very recently been synthesized by a mild evaporation-induced self-assembly method using 1-hydroxyethane-1,1-diphosphonic acid or EDTMPS as organophosphorus coupling molecule and triblock copolymer (F127, P123) or surfactant cetyltrimethylammonium bromide (CTAB) as structure-directing agent, which exhibited their potential for liquid-phase adsorption of heavy metal ions such as Cu²⁺ ions in water and gas-phase adsorption of CO₂ [18–20]. The organophosphonate groups were proved to be homogeneously distributed in the titanium phosphonate framework, however it could not completely exclude the possible existence of titania nanocrystallites. In fact, in practical catalytic applications, doping the metal oxide with small amounts of foreign anions or cations or combining it with another metal oxide is often empirically observed to improve the overall catalytic efficiency of metal oxides and supposed to act as a crystal phase and/or surface area stabilizer [21,22]. Mesoporous titania-based binary oxides such as TiO₂–SiO₂ [23–25], TiO₂–ZrO₂ [26] and TiO₂–CeO₂ [27], and phosphated [28] and phosphonated [8,9] titanias have been found to

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present the enhanced photocatalytic efficiency by retarding the phase transformation of titania and increasing its surface area and surface acidity. Of these reported binary or multiple component compounds, silica was the most widely used one due to its various applications as support for gas adsorption, especially for CO₂ adsorption after modification, and heterogeneous catalysis. In this paper, mesoporous titania–silica–phosphonate (TSP) triconstituent organic–inorganic hybrid materials with different silica content were synthesized through one-pot microemulsion approach using cationic cetyltrimethylammonium surfactant as template and claw-like ethylenediamine-bridged tetra(methylene phosphonic acid) as organophosphorus coupling molecule. The integration of silica in titania–phosphonates improved the regularity of mesostructure and textural property of the resultant mesoporous TSP materials, making them strong adsorption capability for both gas-phase adsorption (e.g. CO₂) and liquid-phase adsorption (e.g. heavy metal ions).

2. Experimental

2.1. Material preparation

Titanium tetrachloride (TiCl₄) was obtained from Tianjin Kermel Chemical Co. EDTMPS was received from Henan Qingyuan Chemical Co. CTAB and tetraethyl orthosilicate (TEOS) were obtained from Tianjin Fine Chemical Co., Ltd. Cyclohexane was provided by Tianjin Jiangtian Chemical Co., Ltd. All chemicals were used as received without further purification. In a typical synthesis, 0.0027 mol of CTAB and 0.00125 mol of EDTMPS were dissolved in 30 mL of deionised water, to which 0–0.02 mol of TEOS was added under stirring. After 5 min, 30 mL of cyclohexane was added into above solution, followed by constant stirring for another 30 min. 0.0025 mol of TiCl₄ was then added dropwise under vigorous stirring. Yellowish precipitation formed immediately and this was kept at room temperature for 60 min before transferred into an autoclave for one-day-aging at 110 °C. The yellow products were filtered, washed with water and ethanol, and dried at 80 °C, followed by extraction of 0.3 g of obtained solid in 100 mL of ethanol solution containing 1.5 mL of concentrated HCl under stirring for 6 h at room temperature to remove surfactant species. The obtained samples were denoted as TSP-*x*, where *x* represented the molar ratio of Si/Ti in the synthesis mixture. To explore the crystalline phase transformation of as-synthesized samples under different calcination temperature, the representative sample TSP-0 was calcined in air at 750 and 825 °C for 3 h with heating rate of 1 °C/min and dwell time of 2 h at 300 °C.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with CuK α radiation, operated at 40 kV and 100 mA. Transmission electron microscopy (TEM) was carried out on a Philips Tecnai G20 at 200 kV. The SEM photomicrographs of the sample was taken out on a Shimadzu SS-550 microscope at 15 keV. N₂ adsorption–desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 120 °C overnight prior to the measurement. The surface areas were calculated by the multi-point Brunauer–Emmett–Teller (BET) method, and pore size distribution was calculated from the adsorption branch of the isotherm by the non-local density functional theory (NLDFT) modeling method. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VECTOR 22 spectrometer with KBr pellet technique. Diffuse reflectance UV–vis absorption spectroscopy was employed on a TU-1901 spectrophotometer

using BaSO₄ as a reference. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a TA SDT Q600 instrument at a heating rate of 5 °/min using α -Al₂O₃ as the reference under air flow of 100 mL/min. The chemical compositions of Si, Ti and P in the sample were analyzed by inductively coupled plasma (ICP) emission spectroscopy on a Thermo Jarrell-Ash ICP-9000 (N + M) spectrometer.

2.3. CO₂ adsorption measurement

Carbon dioxide sorption capacities were determined by a thermogravimetric balance using a TA SDT Q600 analyzer under ambient pressure. The sample was first activated by heating to 110 °C under an inert gas (N₂) flow to remove adsorbed moisture, ethanol and gases and then cooled to 30 °C in inert gas. During the sorption experiment the sample was purged with CO₂ (20 cm³/min). Upon introduction of the gas a weight gain was observed due to CO₂ physical absorption on the sample surface. CO₂ uptake of the samples was tested as well at 30, 50 and 75 °C, respectively.

2.4. Heavy metal ion adsorption

Cd²⁺ ion adsorption test of the hybrid mesoporous materials was performed similar with the method described elsewhere [9]. 10 mg of adsorbent was added to 25 mL of homoionic solution containing different concentration (5, 10, 20, 30, 40 mg/L) of Cd(NO₃)₂. The mixture was stirred for 12 h at room temperature and then filtered. The residual metal ion concentration in the filtrate was analyzed by graphite furnace atomic absorption spectroscopy (AAS). The percent adsorption of metal ion was calculated by the following Eq. (1):

$$\text{Adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where *C_i* and *C_f* are the initial and final metal ion concentrations, respectively.

3. Results and discussion

3.1. Material synthesis and characterization

By using TEOS, TiCl₄ and EDTMPS as the silica, titania and organophosphorus sources respectively, mesoporous TSP hybrid materials with different Si/Ti molar ratios were synthesized in the CTAB/cyclohexane/H₂O microemulsion system, in which the molar ratio of EDTMPS to TiCl₄ was kept as 1:2. The molar ratio of Si/Ti in the synthesis mixture was adjusted to be 4:1, 1:1 and 0, and the resultant samples were marked as TSP-4, TSP-1 and TSP-0, respectively. Since the hydrolysis rate of TiCl₄ is faster than that of TEOS, TEOS was added into the mixed solution of CTAB and EDTMPS prior to TiCl₄. The increase of the acidity due to the hydrolysis of TiCl₄ would accelerate the hydrolysis of TEOS, favor the condensation and cross-linking of silica [29,30], and thus the homogeneous reaction of TiCl₄ and TEOS together with EDTMPS is available, resulting in the aggregation of mesostructured titania–silica–phosphonate nanoparticles around the surfactant/cyclohexane/water microemulsions. The atomic compositions of samples were analyzed by ICP, showing 21.03% Si, 3.45% P and 0.69% Ti (in mass) for TSP-4, and 11.06% Si, 5.07% P and 2.68% Ti (in mass) for TSP-1. The molar ratios of Si/Ti in the resultant samples are larger than that in their initial synthesis gel, which is probably due to the different dissolution of Ti⁴⁺ and Si⁴⁺ species in the synthesis mixture, resulting in the presence of silica oligomers in the resultant samples, besides the homogeneous incorporation of Si in the framework of titania–phosphonate.

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