Super-micropore/small mesopore composite pillared silicate and aluminosilicate materials from crystalline layered silicate Na-RUB-18

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ABSTRACT

We describe the preparation of pillared silicate and aluminosilicate materials with porosity that combines supermicropores and small mesopores. The materials consist of a pillared material that is intercalated within and surrounded by one or several layers of the layered silicate RUB-18. The crystallinity of the RUB-18 is retained when templating surfactant molecules that direct formation of the porous material in the inter-layer region of the host Na-RUB-18 silicate are removed via extraction with acidified ethanol or oxidation with H_2O_2. Calcination, on the other hand generates ordered porous materials that do not exhibit any crystallinity. The porosity of the expanded materials was found to be stable to hydrothermal treatment (i.e., refluxing in water). On calcination, pillared materials that were previously extracted or oxidized, were also found to retain their porosity.

1. Introduction

Pillaring of layered silicate materials is an attractive method for obtaining porous materials with tailored porosity [1–4]. Pillared silicates are interesting due to their potential use as adsorbents, heterogeneous catalysts/catalyst supports, composite materials and molecular sieves [1–8]. The pores of pillared materials may be controlled by the height and number of pillars between layers [9,10]. Among materials that are amenable to pillaring (or inter-layer expansion via ion exchange) are layered silicic acids [4,5] and their derivatives such as magadiite [11,12], kenyaite [13], ilerite [14], and kanemite [15]. In pillared silicates, the rigid silicate framework and pillars combine to generate porous structures with molecular sieving properties [16]. The pore structure of pillared layered materials can be tailored by varying the nature of the host framework and the type of pillaring species, which makes pillaring an attractive method for designing new types of porous materials for targeted molecular sieving, adsorption or catalytic applications [1–8,17].

In 1992, the M41S family of ordered mesoporous silicates, which are prepared via a surfactant templating mechanism was reported [18,19]. At about the same time, Yanagisawa and co-workers reported the synthesis of high surface area mesoporous silicas from kanemite via ion exchange with alkyltrimethylammonium ions [20]. The kanemite-based synthesis method was also used to prepare well ordered mesoporous materials via a 'folded sheet' formation mechanism [21]. In other attempts to prepare pillared layered silicates, Sprung et al. synthesized materials with surface area of 100–200 m^2/g by intercalation of organosilicon compounds such as phenyltrichlorosilane and cyclohexyltrichlorosilane into H-magadiite [22], while Landis and co-workers used inter-layer hydrolysis of tetraethylorthosilicate (TEOS) in primary-organoammonium-exchanged layered silicates to prepare silica pillared materials from magadiite and kenyaite with surface area of 530 and 600 m^2/g, respectively [23]. Later, in 1995, so-called porous clay heterostructures (PCHs) were synthesized via the formation of an M41S-type porous silica structure between clay layers [24–27]. Similar materials were obtained by Kosuge and Tsunashima who reported a high surface area (over 1000 m^2/g) PCH-type silica material derived from intercalation of octylamine and TEOS into the layered silicic acid of ilerite [28].

In the formation of PCHs, a hydrolysable silica source is added onto a layered silicate intercalated with surfactant and amine molecules. The amine and surfactant molecules form micellar templates that interact with the polymerised silicate species to form a Si network in the inter-layer region of the layered silicate. Removal of the amine and surfactant molecules generates pores within the inter-layer region, with the M41S-type silicate framework acting as pillars that keep the layers apart. It is now known that to synthesize PCHs with high surface area, firstly there is need for easy access to the inter-layer region of the host layered material, which may be opened up by introduction of an ionic surfactant (via a cation exchange reaction) and then co-surfactant molecules can be intercalated along with the silica species. This results in the surfactant-directed assembly of silica species into a porous net-

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work within the inter-layer region [24–39]. The preparation of PCHs presupposes the formation of a M41S-type porous material within the inter-layer space of the layered host.

In this work, we have investigated the synthesis of pillared silica and aluminosilica materials from the layered silicate, Na-RUB-18. The aim of the work was to explore the pillaring of a highly crystalline silicate that has a favored face-to-face layer orientation and a high stacking order, and the extent to which RUB-18 layers are fully expanded to allow pillaring. In addition, the effect of mode of removal of organics from as-synthesised materials and both the thermal and hydrothermal stability of template-free pillared derivatives was assessed. The structural ordering, crystallinity and porosity of the prepared pillared materials were probed by powder XRD, NMR, IR spectroscopy, nitrogen sorption analysis, thermal analysis and electron microscopy.

2. Experimental section

2.1. Materials synthesis

2.1.1. Preparation of layered silicate Na-RUB-18

The layered silicate was prepared using established procedures [40,41]. Briefly, 0.94 g of NaOH was dissolved in 183.8 g water at 50 °C, followed by addition of 15 g of hexamethylenetetramine ($C_6H_{12}N_4$) and 40 g of sodium trisilicate hydrate ($Na_2Si_3O_7xH_2O$). After 1 h of stirring, the gel was loaded into a Teflon-lined autoclave and heated statically at 100 °C for 1 month. The resulting Na-RUB-18 powder was recovered by filtration, washed with water and ethanol and dried at room temperature.

2.1.2. Preparation of alkylammonium (CTAB) intercalated layered silicate CTAB-RUB-18

18.4 g of cetyltrimethylammonium bromide, CTAB, (99%, Sigma–Aldrich) was added to 1 g of Na-RUB-18 suspended in 100 ml water and stirred for 24 h at 50 °C. The solid product was recovered via filtration, washed with distilled water to ensure removal of excess CTAB (i.e., until pH 7) and air dried at 120 °C.

2.1.3. Preparation of pillared materials from CTAB-RUB-18

Pure silica pillared materials were prepared from CTAB-RUB-18 as follows: CTAB-RUB-18 was infiltrated by primary amine (octylamine) at room temperature under stirring for 20 min. Then, tetraethylorthosilicate (TEOS) was added to give a synthesis gel with molar ratio CTAB-RUB-18:amine:TEOS of 1:2:12, which was stirred for 3 h. The solid products were recovered by filtration, washed with distilled water and air dried at 120 °C. The product was designated as "As-synthesized" (AS).

Aluminosilicate mesophases were prepared from aqueous suspensions of CTAB-RUB-18, aluminium isopropoxide (Al source), octylamine and TEOS. The synthesis gel molar ratio CTAB-RUB-18:amine:TEOS was 1:2:12. Briefly, CTAB-RUB-18 and octylamine were stirred at room temperature for 20 min. followed by addition of a calculated amount of aluminum isopropoxide (to give Si/Al ratio 5, 10, 20 or 50) and stirring for 20 min. TEOS was then added and the resulting suspension was stirred for 3 h, recovered by filtration, washed with distilled water and air dried at 120 °C. The as-synthesized aluminosilicate samples were designated "x-As-synthesized" (x-AS), where x is the Si/Al ratio.

2.1.4. Surfactant removal

(i) H_2O_2-mediated oxidation. In a typical surfactant oxidation process, 0.6 g of as-synthesized silicate or aluminosilicate material was dispersed under stirring into a solution containing 5 ml of H_2O and 12 mg of $FeCl_3.6H_2O$. 50 ml of 30% H_2O_2 was then added drop by drop. After stirring overnight at room temperature, the solid

was recovered by filtration. To ensure the removal of CTAB and octylamine, the procedure was repeated twice. The resulting samples are referred to as "oxidised", and designated x-oxidised (x-OXI), where x = Si/Al ratio.

(ii) Solvent extraction. In a typical extraction process, 0.5 g of the as-synthesized silicate or aluminosilicate material was subjected to refluxing in 60 ml of 4 wt.% HCl/ethanol solution at 60 °C for 3 h. The refluxing procedure was repeated twice to ensure the removal of CTAB and octylamine. The resulting samples are denoted as "extracted" (EXT) and designated x-extracted (x-EXT), where x = Si/Al ratio.

(iii) Calcination. This procedure was applied to both the as-synthesized and surfactant-free samples as follows:

(a) As-synthesized silicate or aluminosilicates materials were calcined at 550 °C under static air conditions for 4 h. The thermally treated samples are referred to as "calcined" (CAL) and designated x-calcined (x-CAL), where x = Si/Al ratio.

(b) Surfactant-free mesoporous silicate or aluminosilicates (i.e. previously extracted or oxidized) were calcined at 550 °C under static air conditions for 4 h. The thermally treated samples were denoted as x-EXT + CAL and x-OXI + CAL, where x = Si/Al ratio.

2.2. Characterization

Elemental composition (Si/Al ratio) was determined using a Philips MiniPal PW4025 X-ray fluorescence (XRF) instrument. Thermogravimetric analysis was performed using a Perkin Elmer Pyris 6 TG analyzer or a TA Instruments SDT Q 600 analyzer at heating rate of 5 °C/min under static air conditions. Powder XRD analysis was performed using a Bruker AXS D8 Advance powder diffractometer or a Philips 1830 powder diffractometer. For both diffractometers, Cu Kα radiation (40 kV, 40 mA), 0.020° step size, and 1 s step time were used. A Bruker optics TENSOR 27 series FT-IR spectrometer was used to obtain IR spectra. Textural properties were determined via nitrogen sorption analysis at −196 °C using a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer. Before analysis, the samples were oven dried at 150 °C and evacuated overnight at 150 °C under vacuum. The surface area was calculated using the BET method for adsorption data in the relative pressure (P/P_0) range from 0.05 to 0.2. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) ∼ 0.99.

3. Results and discussion

3.1. Structural and framework ordering

The XRD patterns of the parent layered silicate material (Na-RUB-18) and pure silica pillared materials are shown in Fig. 1. We note that the XRD pattern of the Na-RUB-18 agrees well with XRD patterns reported in the literature [42]. All the reflections are characteristic of the layered silicate RUB-18, which indicates that the present sample is highly crystalline and free from impurities. The sharp peak at $2\theta = 7.7°$, is assigned to the inter-layer distance (11.1 Å) of Na-RUB-18 [43]. The XRD pattern of CTAB-RUB-18 exhibits an expanded basal (004) peak (26.9 Å) and at least two more (0 0 1) diffractions. The expansion of inter-layer spacing (from 11.1 to 26.9 Å) occurs due to replacement of Na with CTAB (Q^+) ions. The CTAB-RUB-18 material exhibits peaks in the 2θ region between 10 and 40°, which indicate that the crystallinity of RUB-18 layers is retained. The spacings derived from the low angle region of the XRD patterns for all the samples are given in Table 1. The as-synthesized silica pillared material (AS) exhibits several peaks, which correspond to spacing of 42.4 Å, 28.7 Å, 22 Å and 13.6 Å. The peaks at 28.7 Å and 13.6 Å are from unaltered CTAB-