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Novel method to synthesize highly ordered ethane-bridged PMOs under mild acidic conditions: Taking advantages of phosphoric acid

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Highly ordered SBA-15-type ethane-bridged PMOs have been obtained by employing H_3PO_4 as acid to tune the pH in the presence of copolymer surfactant P123. The effects of the acidity and the addition of inorganic salt on the formation of the mesostructure are investigated. It is found that, compared with HCl, the polyprotic weak acid H_3PO_4 is preferable for the synthesis of highly ordered SBA-15-type ethane-bridged PMOs with larger pore size and surface areas under mild acidic conditions. Moreover, taking the advantages of the mild acidic condition, vanadium-containing SBA-15-type ethane-bridged PMOs were successfully prepared through a direct synthesis approach. The XRD, N_2-sorption, UV–Vis and CW-EPR studies of the V-PMO show that part of the vanadium species are present in polymeric $(V{-}O{-}V)_n$ clusters, while part of the vanadium centers are well-dispersed and immobilized on the inner surface of the mesopores.

1. Introduction

Periodic mesoporous organosilicas (PMOs) form a new class of mesoporous materials with highly ordered pore structures and uniformly distributed organic groups inside the siliceous frameworks [1–4]. The combination of the organic and inorganic components gives PMOs some unique properties, such as the tunable surface hydrophobicity, and enhanced mechanical and hydrothermal stability [5]. Moreover, the porous structure, and surface and framework properties of PMO materials can be finely tuned by varying the bridging organic groups and the synthesis conditions. So far, a variety of organic groups has been incorporated into the framework of PMOs, leading to materials with promising applications in many fields, such as the chemical industry (catalysis), environmental applications (metal scavenging) and medical applications (controlled drug release).

In general, PMOs are prepared via the hydrolysis and condensation of bridged silsesquioxane species $(RO)_3Si\text{-}R\text{-}Si(OR)_3$ under basic or acidic conditions in the presence of various structure-directing agents. Most PMOs reported so far have MCM-41- or SBA-15-type mesostructures consisting of uniform one-dimensional channels [6]. In comparison with the MCM-41-type PMOs synthesized with ionic alkylammonium surfactants, SBA-15-type PMOs templated by triblock copolymers surfactant are much more desirable, not only because of the larger pore size and thicker pore walls, but also due to the presence of the unique interconnected pores. Up to now, great effort has been devoted to the preparation of SBA-15-type PMOs. However, due to the different interfacial energy between the precursor and template for silica and organosilica, a precise control of the synthesis conditions is needed for obtaining highly ordered SBA-15-type PMOs in contrast to the easier fabrication of SBA-15 materials. The effect of the SiO_2/template ratio on the properties of the material has been studied by several research groups [7,8]. Bao et al. [9,10] investigated the influence of acid concentration on the degree of structural order and the external morphology of the final product. Burleigh et al. [11] prepared a series of SBA-15-type PMOs with different pore diameter (from 6 to 20 nm) by using 1,3,5-trimethylbenzene (TMB) as the swelling agent. Moreover, the structural order and morphology of these materials could be

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strongly affected by the addition of additives such as inorganic salts [12–14]. Up to now, in most cases, SBA-15-type PMOs are synthesized at a $pH < 1$ using strong acids, like HCl. To our knowledge, there is no report on the synthesis of SBA-15-type PMOs using weak acids. Compared with HCl, H_3PO_4 is a polyprotic weaker acid, and it has been reported for SBA-15 that the use of H_3PO_4 rather than HCl during the self-assembly process could promote changes in the ionic strength and pH at the interface [15]. Using the triblock copolymers surfactant, the self-assembly is governed by weak van der Waals interactions or hydrogen bondings. Hence, tiny modifications of the experimental conditions can lead to significant changes during the self-assembly process and consequently influence the characteristics of the final material. Colilla et al. [16] found that the surface area of SBA-15 can be increased by employing H_3PO_4 as an acid source. Moreover, phosphorus has been successfully incorporated into the framework when a large amount of H_3PO_4 is used. Pitchumani et al. [17] obtained a broader variety of morphology of SBA-15 when using H_3PO_4 compared with that of HCl. In addition, the use of the polyprotic weak acid H_3PO_4 may induce a mild acidic condition, which can be beneficial for the incorporation of metal atoms into the framework of PMO materials.

Vanadium-containing mesoporous materials have been proven to be effective catalysts for many selective oxidation reactions [18–20]. The catalytic activity and selectivity of these vanadium-containing catalysts strongly depends on the nature, location and dispersion of the vanadia in the catalyst [20,21]. Although vanadium-containing mesoporous materials have received considerable attention, the reports on the direct-synthesis of vanadium-containing PMO materials are still very limited. Singh et al. [22] have prepared vanadium-containing ethane-bridged PMOs using cationic surfactants under basic conditions. Furthermore, it was found that vanadium-containing PMOs were highly active and more stable than conventional vanadosilicates during the liquid-phase epoxidation reaction of styrene using aqueous H_2O_2 or TBHP as the oxidants [22]. Recently, a novel type of PMO material embedded with $[VO(acac)_2]$ has been successfully synthesized through a co-condensation method under basic conditions [23]. Nevertheless, all these vanadium-containing PMOs were obtained under basic conditions in the presence of cationic surfactants.

In the present study, we present the synthesis of SBA-15-type ethane-bridged PMOs by employing H_3PO_4. The effects of the acidity and inorganic salt on the formation of the mesostructure are investigated. Moreover, vanadium-containing SBA-15-type PMOs were successfully prepared through a direct synthesis approach. This is the first example of V-PMO synthesized under acidic conditions using non-ionic surfactants. In comparison to the HCl-assisted synthetic pathway, the use of H_3PO_4 is more advantageous for the formation of SBA-15-type ethane-bridged PMOs under mild acidic conditions, both from the point of view of metal incorporation and the structural properties of the final materials.

2. Experimental section

2.1. Materials

All starting materials were used as purchased without further purification: 1,2-bis(triethoxysilyl)-ethane (BTEE, 96% Sigma–Aldrich), Pluronic P123 triblock copolymer (EO_{20}-PO_{70}-EO_{20}, Sigma–Aldrich), H_3PO_4 (85% Acros Organic), HCl (37% Acros Organic), methanol (99.9% Merck KGaA), NaCl (Sigma–Aldrich), $VOSO_4 \cdot 5H_2O$ (Sigma–Aldrich).

2.2. Synthesis of PMO materials

SBA-15-type ethane-bridged PMOs were synthesized from BTEE in the presence of P123 under low acidic conditions, adapting slightly the HCl-based synthesis procedure reported by Bao et al. [9] In a typical synthesis procedure (***PMO 1-7***), 1.04 g P123 was dissolved in 31.5 g of H_3PO_4 solution with a definite concentration (see Table 1). Then, 2 ml BTEE was added into the above mixture at 40 °C and stirred at the same temperature for 24 h. The mixture was then transferred into an autoclave and followed by aging at 100 °C under static condition for another 5 days. The obtained white precipitate was filtered, washed thoroughly with deionized water, and dried at room temperature. Surfactant template removal was accomplished by two solvent extraction cycles with ethanol. Typically, 1 g of as-made PMOs was treated under vigorous stirring for 6 h at 60 °C in 200 ml of ethanol, followed by filtration, washing with ethanol and drying. ***PMO 8-10*** were synthesized under the same pH value with ***PMO 2-5***, but using HCl instead of H_3PO_4. ***PMO 11-13*** were prepared using H_3PO_4 with the assistance of NaCl with the molar ratios of NaCl/BTEE = 8. ***V-PMO*** was synthesized with the same recipe of ***PMO 11***, except for the addition of the vanadium source with the molar ratios of $VOSO_4$/BTEE = 0.06. Table 1 lists the details of the synthesis conditions including the pH value and reactant compositions.

2.3. Characterization

N_2 adsorption–desorption isotherms were obtained at liquid N_2 temperature (77 K) using a Quantachrome Quadrasorb-SI automated gas adsorption system. Prior to adsorption, the samples were outgassed under high vacuum for 16 h at 100 °C. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method, between a relative pressure of 0.05 and 0.35. The pore size distributions (PSD) were deduced from both the adsorption branch and desorption branch of the isotherms using the NLDFT method. The total pore volumes were calculated from the amount of N_2 vapor adsorbed at a relative pressure of 0.95. The micropore area and volume were calculated by the *t*-plot method using experimental points at a relative pressure of $P/P_0 = 0.25$–0.55.

X-ray diffraction (XRD) measurements were recorded on a Pananalytical X'PERT PRO MPD diffractometer with filtered CuKα-radiation. The measurements were performed in the 2θ mode using a bracket sample holder with a scanning speed of 0.04°/4 s in continuous mode. The unit cell parameters (a) were determined from the interplanar spacing of the (100) planes.

Table 1
Synthetic details of the PMOs under study.

No.	pH	Acid concentration	H_3PO_4/BTEE	P123/BTEE	H_2O/BTEE
PMO-1	2.1	0.48×10^{-3}M	0.16	0.034	336
PMO-2	2.0	0.72×10^{-3}M	0.24	0.034	336
PMO-3	1.8	0.96×10^{-3}M	0.32	0.034	336
PMO-4	1.5	0.19×10^{-2}M	0.64	0.034	336
PMO-5	1.2	0.38×10^{-2}M	1.28	0.034	336
PMO-6	0.8	0.77×10^{-2}M	2.56	0.034	336
PMO-7	0.5	1.54×10^{-2}M	3.84	0.034	336
PMO-8[a]	2.0	N.A.	N.A.	0.034	336
PMO-9[a]	1.8	N.A.	N.A.	0.034	336
PMO-10[a]	1.5	N.A.	N.A.	0.034	336
PMO-11[b]	2.3	0.24×10^{-3}M	0.08	0.034	336
PMO-12[b]	2.1	0.48×10^{-3}M	0.16	0.034	336
PMO-13[b]	2.0	0.72×10^{-3}M	0.24	0.034	336

[a] Materials obtained by tuning pH with 1 M HCl.

[b] Materials obtained with the assistance of NaCl with a molar ratio of NaCl/BTEE = 8.