

Pergamon

PII S0025-5408(98)00147-0

MESOPOROUS SILICOPHOSPHATES

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> (Communicated by M. Greenblatt) (Received February 4, 1998; Accepted February 4, 1998)

ABSTRACT

Mesoporous silicophosphates containing up to 22% phosphorus were prepared using cationic surfactants. A mesoporous silicophosphate of the approximate composition $Si_{19}P_4O_{48}$ had a surface area of 770 m²g⁻¹, after removal of the template. A thermal transformation from a lamellar to a hexagonal structure was observed in this solid. The mesoporous silicophosphate phases were characterized by infrared and NMR spectroscopy. © 1998 Elsevier Science Ltd

KEYWORDS: A. ceramics, A. microporous materials, D. catalytic properties, D. surface properties

INTRODUCTION

Since the first reported synthesis of mesoporous silica [1], several mesoporous oxides have been prepared using ionic as well as neutral templates [2]. Some examples of these are ZrO_2 [3], TiO₂ [4], SnO₂ [4], Al₂O₃ [5], and Nb₂O₅ [6]. Mesoporous aluminophosphate [7] and aluminoborate [8], which are analogous to silica, have also been prepared and characterized. We were interested in investigating whether mesoporous silicophosphates could be prepared by using suitable templates. Crystalline and glassy silicophosphates are known, and in some of them, silicon occurs with octahedral coordination [9–11]. Silicophosphates find applications as hosts for fast ionic conductors and optical fibers [11] and as catalysts [12]. In this communication, we report the successful synthesis of mesoporous silicophosphates with various phosphorus content, by using cationic surfactants.

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| mesoporous sincophosphales | | | | | |
|----------------------------|-------------------------------------|--------------|-----|---|---|
| Sample | Preparative condition | | | | |
| | Acid (mmol) | SA (mmol) | pН | Composition ^a | Surface area ^b (m^2g^{-1}) |
| 1 | H ₃ PO ₂ (18) | CTAB(8) | 11 | SiO ₂ ·0.1SA | 1100 |
| 2 | $H_{3}PO_{4}(22)$ | CPB(7) | 3.5 | 23SiO ₂ ·P ₂ O ₅ ·3.8SA·3H ₂ O | 965 |
| 3 | $H_{3}PO_{2}(18)^{c}$ | CPB(7) | 3.5 | 9.4SiO ₂ •P ₂ O ₅ •3.0SA•1H ₂ O | 770 |
| 4 | $H_{3}PO_{2}(22)$ | CTA(8) | 3.5 | 3SiO ₂ ·P ₂ O ₅ ·0.9SA·0.7H ₂ O | 130 ^d |

TABLE 1 Mesoporous Silicophosphates

^aOf the as-synthesized material.

 b Of the samples calcined at 673 K. In sample 3, over 80% of the template was removed on calcination.

 $^{c}H_{3}PO_{2}$ with CTAB under similar conditions gave a product with 7% P. ^{d}Not mesoporous.

EXPERIMENTAL

In the preparation of mesoporous silicophosphates, we used tetraethylorthosilicate (TEOS) and phosphoric or phosphinic acid as the starting materials and cetyltrimethlammonium bromide (CTAB) and cetylpyridinium bromide (CPB) as the surfactants (SA). The preparation was carried out in acidic media, unlike that of silica, which is carried out in a basic medium. In a typical synthesis, 7–8 mmol SA were added to water. This solution was stirred for 20 min, then 2.8 mL HCl (5.6 M) was added. TEOS (16 mmol) was added to the SA solution, with stirring for 15 min, followed by the addition of H_3PO_4/H_3PO_2 (~20 mmol). The pH of the resulting mixture was adjusted to 3.5 by adding 5 M NaOH solution, and stirring continued until a gel was obtained. The gel was aged at ambient temperature for 20 h. The final product was filtered and dried at 373 K for 4 h.

Thermogravimetric analysis (TGA) of the dried product was carried out using a Mettler-Toledo TG850 instrument. Energy dispersive X-ray (EDX) analysis was performed with a Leica scanning electron microscope. X-ray diffraction (XRD) patterns were recorded with a Rich Seifert instrument. Transmission electron microscopy (TEM) images were obtained with a Jeol JEM-3010 instrument.

RESULTS AND DISCUSSION

The various compositions prepared by us, together with some preparative details are listed in Table 1. From this table, we see that phosphorus was incorporated into all the preparations carried out at a pH of 3.5. Higher pH led to the formation of pure mesoporous silica, independent of the presence of an initial excess of H_3PO_4/H_3PO_2 . The extent of the incorporation of phosphorus depended on the phosphorus source and the SA; H_3PO_4 -CTAB and H_3PO_2 -CPB combinations seemed to favor the incorporation. We also found that the bromide of the SA was exchanged by chloride from HCl during the preparation. Without the addition of HCl, however, we failed to obtain the silicophosphates.

In Figure 1, we show the XRD patterns of the as-synthesized mesoporous silicophosphates samples 3 and 4 along with the XRD pattern of the mesoporous hexagonal phase of silica



FIG. 1

XRD patterns of the as-synthesized silicophosphates samples (1, 3, and 4) and the calcined samples of 1 and 3. For a description of the compositions, see Table 1.

(sample 1) with a d_{100} of 3.87 nm. The diffraction patterns of samples 3 and 4 are quite similar to that of silica, giving the (100) reflection at *d* values between 3.8 and 3.9 nm. The XRD pattern of sample 3 has some features of the lamellar phase, and TEM images show the presence of the hexagonal phase admixed with a small proportion of the lamellar phase. Calcination of the samples at 673 K for 4 h removed most of the surfactant, as determined by TGA and elemental analysis. Infrared spectra showed the near-absence of the bands of the template. The mesoporous structure was fully retained in samples 1, 2, and 3 after calcination at 673 K, as seen from the XRD patterns (see Fig. 1). The mesoporous structure of sample 4 (with ~40% P), however, was destroyed on calcination at 673 K. The phosphorus content of the silicophosphates after calcination was Close to the values given in Table 1. The composition of sample 3 after calcination was Si₁₉P₄O₄₈. It appears that silicon can be substituted up to a maximum of 25% by phosphorus, in the hexagonal mesophorous phase.



FIG. 2

TEM image of silicophosphate sample 3 (a) during calcination and (b) after calcination at 673 K.

The BET surface areas of samples 1, 2, and 3 calcined at 673 K were 1150, 965, and 770 m^2g^{-1} , respectively.

It was mentioned earlier that sample 3 contained a mixture of lamellar and hexagonal forms. On heating at 673 K, the lamellar phase transformed into the hexagonal phase. In Figure 2, we show the TEM images of sample 3 (with 22% P) to demonstrate the presence of both the lamellar and hexagonal phases during transformation and the crystalline nature of the fully transformed hexagonal phase. Such a lamellar-to-hexagonal transformation in the solid state is interesting. It appears that the transformation is favored by the partial elimination of the template on heating the lamellar phase, which enables the structure to curl up to produce the cylindrical structure.

The TGA curves, chemical analysis, and compositional dependence of the thermal stabilities of the mesoporous structures indicated that phosphorus was incorporated into the silica framework. Further evidence of the incorporation of phosphorus was obtained by NMR and infrared spectroscopy. We examined the ³¹P and ²⁹Si MAS NMR spectra of the mesoporous silicophosphates. Both spectra changed during calcination in the case of sample 3, as shown in Figure 3. The ³¹P signals of the calcined sample 3 (relative to H₃PO₄) are at –13.0, –23.1, and –34.4 ppm due to OP(OSi or P) (OH)₂, OP(OSi or P)₂ (OH), and OP(OP)_{3-x}(OSi)_x,



FIG. 3

²⁹Si and ³¹P MAS NMR spectra of sample 3 (a) before and (b) after calcination.

respectively [11]. The ²⁹Si signals of this silicophosphate are at –91 (Q₁, Q₂), –104 (Q₃) and –111 ppm (Q₄) [10,13,14], the slight shift to negative values arising from the incorporation of phosphorus. It appears that silicon was present only as a 4-coordinated species in these silicophosphates. The infrared spectrum of calcined sample 3 showed a strong band at 1080 cm⁻¹ due to a coupled Si–O and P–O stretching vibration. Bands due to the bending vibration of Si–O–P/Si–O–Si/P–O–P units are found at 815 and 455 cm⁻¹ [15]. Thus, the present study demonstrated that the mesoporous phases of silicophosphates in which phosphorus is an integral part of the silica framework can be prepared. The use of these materials as hosts in catalysis is being explored.

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