# Thermally stable macroporous zirconium phosphates with supermicroporous walls: a self-formation phenomenon of hierarchy†

Tie-Zhen Ren, Zhong-Yong Yuan and Bao-Lian Su*

*Laboratory of Inorganic Materials Chemistry, The University of Namur (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium. E-mail: bao-lian.su@fundp.ac.be; Fax: +32-81-725414; Tel: +32-81-4531*

A self-formation phenomenon leading to the hierarchically thermally stable macroporous zirconium phosphates with amorphous supermicroporous walls from the precursors of zirconium propoxide and orthophosphoric acid solution was observed.

The rational design and synthesis of hierarachically porous structures at multiple length scales are one of the most important current interests,[1] because among the potential applications for manipulated, mass manufactured hierarchical materials with different pore sizes integrated in one body are to combine reduced resistance to diffusion and high surface areas for yielding improved overall reaction and adsorption/separation performances which can be extended to biological applications. Our earlier work was based on the use of one surfactant to direct the formation of both mesoporous and macroporous structures of metal oxides and aluminosilicates,[1] which was distinct from the previously reported methods of dual-templating, *i.e.* the combination of surfactant templating techniques and micromoulding methods of emulsion droplets, colloid crystals, or bacterial threads for the construction of hierarchically mesoporous–macroporous oxide materials.[2] Herein, we describe a self-formation phenomenon, a novel and facile templateless, surfactantless preparation of hierarchically supermicroporous–macroporous zirconium phosphate (ZrPO) materials.

Zirconium phosphate is one of the most studied members of the well-known family of layered solid acids,[3] and its proton conductivity,[4] ion-exchange and adsorption,[5] and catalytic activity[6] have been widely studied. Surfactant-assisted methods have been used to prepare porous ZrPOs of mesophases for potential application as catalysts and catalyst supports.[7] Highly ordered, stable mesoporous ZrPOs were reported by Zhao *et al.* very recently based on an 'acid–base pair' route by using a triblock copolymer as a template.[8] The present communication is the first description of a new form of hierarchically porous ZrPO materials possessing a uniform macroporous structure with supermicroporous walls, which should be significant from a technological point of view. The synthesis process is quite simple without the use of any templating agents, and extendable to the synthesis of other metal phosphate materials of hierarchical nanoporous structures and bioactive membranes.

In a typical self-formation procedure, 0.01 mol of zirconium *n*-propoxide ($Zr(OC_3H_7)_4$, 70 wt.% solution in 1-propanol, Aldrich) was added dropwise into a pre-treated 60 mL solution of orthophosphoric acid (0.1 mol $L^{-1}$) under stirring. After a further stirring of 2 h at room temperature, the obtained mixture was separated into two parts: one was transferred into a Teflon-lined autoclave and aged statically at 80 °C for 24 h (denoted as ZrP-h), and another was directly filtered, washed with water, and dried at 60 °C (denoted as ZrP-d) for comparing. The obtained white ZrP-h solid was then calcined at 500, 650 or 800 °C for 1 h, denoted as ZrP-hc500, ZrP-hc650 and ZrP-hc800 respectively, to investigate the thermal stability.

Fig. 1 shows the $N_2$ adsorption–desorption isotherms of the ZrP-h sample and its calcined products and their corresponding pore size distribution curves. Both the as-prepared and calcined products exhibit the isotherms of type IV. The adsorption isotherms present a high uptake of $N_2$ at low relative pressure ($P/P_0$) of 0.1–0.40, indicating the presence of supermicropores with the pore size ranging from 1–2 nm (between micropore and mesopore size). The analysis of the pore size distribution by the Barret–Joyner–Halenda (BJH) method from the adsorption branch of the isotherms reveals a narrow pore size distribution centered at 1.7 nm for a ZrP-h sample, and pore sizes of 1.4–1.7 nm for the calcined samples (Table 1). Meanwhile, at the relative pressure higher than 0.85, a strong increase in nitrogen adsorbed volume is observed, evident of an appreciable amount of secondary porosity, *i.e.* the large mesopores or macropores. This secondary porosity, as well as the uniform supermicroporosity, can be clearly seen in the sample calcined even at 800 °C. A very high specific surface area of 528 $m^2$ $g^{-1}$ is obtained with pore volume of 0.572 $cm^3$ $g^{-1}$, which is comparable to that of previously reported surfactant-templated meso-macrostructured $ZrO_2$,[9] and practically higher than that of the triblock copolymer-templated large-pore mesoporous ZrPO material.[8] Although the surface areas and pore volumes decrease with the increase of the calcination temperature (Table 1), a high surface area of 132 $m^2$ $g^{-1}$ with a pore volume of 0.232 $cm^2$ $g^{-1}$ and a narrow pore size distribution centered at 1.7 nm can still be obtained after calcination at 800 °C, suggestive of the very high thermal stability of the present materials. It is also noted that both as-prepared and calcined samples presented a small quantity of microporosity (Table 1), revealed by the *t*-plot analysis.

The SEM and TEM images of the synthesised ZrPO materials are shown in Fig. 2, which reveal a uniform macroporous structure. A regular array of the macropores with the diameters ranging from 300 to 800 nm is seen. The hollow macrochannels are practically parallel to each other, and extend throughout almost the whole particles (ESI†). A close observation shows that the macropores themselves are also hierarchical (Fig. 2b), *i.e.* an unusual form of 'macropores-in-macropores'.[10] The regularity of macropores is further confirmed by the cross-sectional TEM images (Fig. 2c). The high-magnification TEM images also reveal that the macroporous
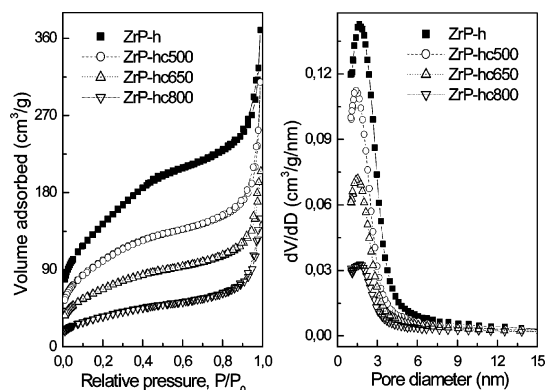


**Fig. 1** $N_2$ adsorption–desorption isotherms (left) and the corresponding pore size distribution curves (right) of the hierarchical ZrPO samples.

**Table 1** Textural properties of the as-prepared hierarchical porous ZrPO materials and their calcined products at different temperatures

| Sample | $S_{BET}^{a}/$ m$^2$ g$^{-1}$ | $V_{pore}^{b}/$ cm$^3$ g$^{-1}$ | $D_{ads}^{c}/$ nm | $D_{des}^{d}/$ nm | $S_{micro}^{e}/$ m$^2$ g$^{-1}$ | $V_{micro}^{e}/$ cm$^3$ g$^{-1}$ |
|---|---|---|---|---|---|---|
| ZrP-h | 528 | 0.572 | 1.7 | 1.8 | 24 | 0.001 |
| ZrP-hc500 | 369 | 0.478 | 1.4 | 1.3 | 72 | 0.025 |
| ZrP-hc650 | 248 | 0.317 | 1.5 | 1.5 | 43 | 0.014 |
| ZrP-hc800 | 132 | 0.232 | 1.7 | 1.6 | 8 | 0.001 |
| ZrP-d | 200 | 0.251 | — | — | 106 | 0.048 |
| ZrP-dc500 | 72 | 0.254 | — | — | 16 | 0.006 |

[a] BET surface areas. [b] Nitrogen pore volumes at $P/P_0 = 0.993$. [c] BJH pore diameter determined from the adsorption branch. [d] BJH pore diameter determined from the desorption branch. [e] Microporous surface area and pore volume determined by the $t$-plot analysis.
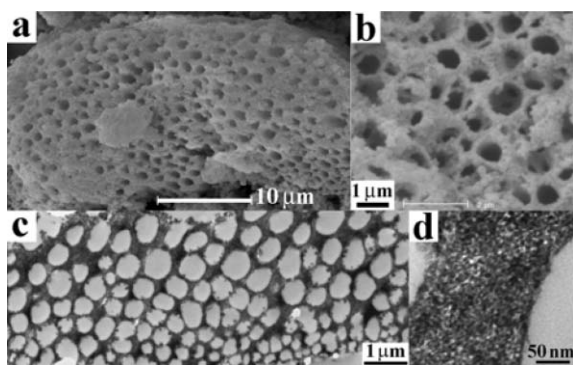


**Fig. 2** (a, b) SEM and (c, d) cross-sectional TEM images of the ZrP-h.

framework is mesostructured with a disordered wormhole-like assembly of accessible meso/micropores (Fig. 2d), which is in agreement with the uniform supermicroporosity revealed by N$_2$ adsorption analysis. The macroporous structure, confirmed by TEM and SEM images, should be related to the secondary porosity observed in the N$_2$ adsorption isotherms. It is substantially significant that such a hierarchically supermicroporous–macroporous structure is thermally stable, even after calcination at 800 °C (ESI†). In contrast, the previously reported surfactant-templated meso-macroporous ZrO$_2$ structure was only stable up to 300 °C.[9]

The non-autoclaved ZrPO sample, ZrP-d, shows a lower surface area than the autoclaved ZrP-h (Table 1). There is no supermicroporosity or mesoporosity observed for ZrP-d, though a similar macroporous structure could be seen with low quantity (ESI†). This indicates that the self-formation of macroporous structure was spontaneously initiated before the autoclaving of the reaction system. The hydrolysis of Zr-alkoxide precursors in the phosphate solution would result in the rapid formation of nanometer-sized ZrPO particles. A lot of propanol molecules were quickly and simultaneously generated by the reaction of zirconium propoxide and phosphatic ions and the polycondensation, which might produce microphase-separated domains of ZrPO-based nanoparticles and water/alcohol channels[11] that are the initiators of the macrochannels. Autoclaving will consolidate the regular self-assembly of the nanoparticles, creating a well-connected network of narrow supermicroporous channels. Thus, a hierarchical structure of uniform macrochannels with supermicroporous walls of nanoparticle assembly would self-form during the synergistic packing of the nanoparticles and rapid release of propanol molecules.

Both the as-prepared and calcined ZrPO samples possess amorphous framework walls, as revealed by X-ray diffraction patterns (Fig. 3). No crystallized ZrPO$_4$ or ZrO$_2$ phases appear even after calcination at 800 °C. The $^{31}$P MAS NMR spectra of
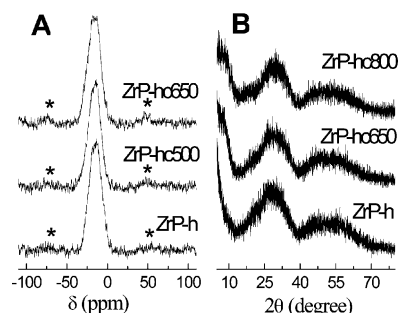


**Fig. 3** (A) $^{31}$P MAS NMR spectra and (B) X-ray diffraction patterns of the synthesized ZrPO samples. Asterisks indicate the spinning sidebands.

both as-prepared and calcined ZrPOs show the peaks between $-12$ and $-19$ ppm (Fig. 3), which may be attributed to tetrahedral phosphorus atoms bonded to four or less ZrO$_4$ units.[12] Calcination did not result in the shift of the $^{31}$P NMR signals, suggestive of the stable coordination environment of phosphorus. Infrared spectroscopic characterization also reveals the presence of acid sites in these ZrPO samples.

Therefore, hierarchically macroporous zirconium phosphate materials with amorphous supermicroporous walls, possessing high thermal stability, have been prepared by a simple self-formation route. It is believed that, due to their attractive properties, such hierarchical materials should be significant and possess great potential for practical application in the fields of catalysis and materials science.

## Notes and references

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