Uniform core-shell titanium phosphate nanospheres with orderly open nanopores: a highly active Brønsted acid catalyst[†]

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We have successfully designed and synthesized core-shell multicomponent TiP nanospheres with a stable crystal core and orderly open nanopores, which have uniform distribution and good dispersion and offer great potential as a highly active Brønsted acid catalyst.

Open framework microporous/mesoporous nanomaterials with various architectures have been obtained through new chemical approaches in the last two decades.¹⁻³ Many applications based on these structures have been proposed due to their excellent properties including high surface area, high selectivity, ordered framework and excellent catalytic activities.^{1,2,4} Although metal phosphates are considered to be ideal catalysts or catalyst supports which are much more easily separated and recycled than liquid acids,⁵ their catalytic efficiencies may be restricted by the low effective surface area and long detention time of reactants, due to big aggregates, smaller pore size and long-capillary nanopores. Therefore, size distribution and pore shapes of solid catalysts and their ability to disperse in the solvent are very important properties. Thus far, the design of novel open nanoporous nanocatalysts with good dispersion and thermal stability is still a great challenge.

Titanium phosphates (TiPs) have attracted interest as efficient solid acid catalysts in recent years.^{6–10} Many microporous/mesoporous TiPs have been synthesized with the aid of surfactants or small organic molecules.^{11–15} In previous work, microporous TiP nanospheres were obtained by using calf thymus DNA as a structure-directing agent, but it is not appropriate for multi-gram scale synthesis.⁷ Very recently, titanium phosphate-modified SBA-15 with orderly nanopores was synthesized by layer-by-layer liquid-phase grafting methods.¹⁶ However, to the best of our knowledge, few practical and short routes have been reported to synthesize TiP nanomaterials with uniform size distribution, open nanopores and good dispersion. Herein, we report a facile method to prepare core–shell multicomponent TiP nanospheres with more effective surface area and open nanopores. The TiP nanocatalysts have a stable crystal core framework, uniform size distribution, good dispersion and orderly nanopore distribution, and present high Brønsted acid activity and selectivity for ketalization reactions with up to 96% yield and 100% selectivity.

We synthesized TiP nanospheres using docusate sodium salt (AOT), orthophosphoric acid (85%) and titanium(IV) *n*-butoxide as the starting materials. AOT as sodium source and structure-directing agent was first added into ethanol to prepare AOT/ethanol solution. After phosphoric acid was added, a precipitate (NaH₂PO₄) was obtained because of its restricted solubility in the ethanol solution, and then the precipitate was removed to control the sodium concentration in the solution. On tetrabutyl titanate/ethanol solution being added, sodium titanium phosphate crystal cores (first TiP component) were formed. Then the second TiP component began to grow on their surface. Terminal groups (H₂PO₄)⁻ were obtained due to the presence of excess phosphoric acid in the solution. Finally, a white solid powder was obtained after washing, separation and drying.

The morphology of TiP samples calcined at different temperatures was characterized by an electron microscope method. A field emission scanning electron microscopy (FESEM) image and size distribution curve of the products as synthesized at 80 °C are presented in Fig. 1a, which show that TiP nanospheres with uniform dispersion were obtained and the diameters of TiP nanospheres are about 50 nm. After calcination at 400 °C, open nanoporous TiP nanospheres, which were formed by using AOT as a structure-directing agent, are clearly shown in Fig. 1b.

The XRD powder patterns of TiP samples after annealing at 100, 200 and 400 °C are displayed in Fig. 2a. All diffraction peaks of the as-synthesized sample at 100 °C are indexed to the NaTi₂(PO₄)₃ phase (JPCDS No. 33-1296), suggesting that crystalline NaTi₂(PO₄)₃ was formed as the only crystal component in the product. This is supported by the X-ray photoelectron spectroscopy data which show the main elements including Na, Ti, P and O as shown in Fig. S1a.⁺ After calcination at 200 °C or 400 °C, the XRD patterns of TiP samples have not obviously changed compared to the patterns at 100 °C, which shows the thermal stability of the TiP crystal component. The TiP samples were proved to be multicomponent TiP by XRD data as shown in Fig. S1b.† After treatment at 600 °C, the crystalline NaTi₂(PO₄)₃ is still stable and a new crystal phase (TiP₂O₇, JPCDS No. 38-1468) was formed with the loss of chemical water in the Ti(HPO₄)₂ component.

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Fig. 1 (a) FESEM image of as-synthesized TiP sample and its particle size distribution curve (inset); (b) TEM image of the product annealed at 400 °C.



Fig. 2 (a) XRD patterns of TiP samples at 100, 200 and 400 $^{\circ}$ C; (b) N₂ adsorption–desorption isotherms of TiP sample annealed at 400 $^{\circ}$ C (inset: corresponding pore-size distribution curve).

 N_2 adsorption–desorption isotherms and pore size distributions of samples are shown in Fig. 2b. The BET surface area of TiP material calcined at 400 °C is 305 m² g⁻¹. The average

pore diameters of TiP materials are 14 Å and 28 Å, respectively as calculated using density functional theory and the shape of the nanopores is deduced to be a gradient structure based on the broad pore distribution. The adsorption isotherm is similar to Langmuir single layer absorption and the hysteresis of the desorption isotherm begins at *ca.* $p/p_0 =$ 0.85. This indicates that the material has short open gradient nanopores in which N₂ molecules have a shorter dwell time than that in the long capillary of molecular sieves which was usually filled starting from $p/p_0 = 0.4$.¹¹ The open nanoporous structure which supports the electron microscope analysis implies that more effective catalytic active sites may be exposed on the surface of TiP nanospheres and the residence time of reactant in TiP nanopores could be shortened.

A direct proof of the components of TiP nanospheres is ³¹P Cross Polarization/Magic-Angle Spinning (CPMAS) spectra shown in Fig. S2a,† which provide evidence that the as-synthesized product consists of $(PO_4)^{3-}$, $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ with relative chemical shifts at -26.4 ppm, -19.1 ppm and -10.9 ppm respectively.^{17,18} The peak at -26.4 ppm is assigned to NaTi₂(PO₄)₃ which proves a stable crystalline core could be prepared with high crystallinity; the other three broad peaks formed are due to the noncrystallinity of TiP shell components which is the reason why only the NaTi₂(PO₄)₃ component is present in the XRD data for the as-prepared products. The two main components, Ti(HPO₄)₂ (shell) and NaTi₂(PO₄)₃ (core), which are very stable even after calcination at 450 °C, are further proved by ³¹P spectra in Fig. S2b.†

Fig. 3 shows the ¹H MAS solid NMR spectra of TiP nanospheres. The spectrum contains three main peaks at 8.97 ppm, 4.27 ppm and 1.70 ppm respectively at 100 °C.^{19,20} The strongest peak at 8.97 ppm can be attributed to chemically adsorbed protons on the surface of the sample, largely due to the formation of P–OH groups in $H_2PO_4^-$ or HPO_4^{2-} components. The sharp peaks at 4.27 ppm and 1.70 ppm originate from physically absorbed or crystal water and C–H of AOT surfactant respectively, whereas these two peaks of the annealed product at 250 °C almost disappear due to the decomposition of surfactant and loss of H₂O. Though the peak becomes smaller after calcination at 600 °C, many Brønsted acid sites (P–OH groups) still exist in the sample.



Fig. 3 ¹H MAS NMR spectra of TiP samples calcined at different temperatures (100, 150, 200, 250, 300 and 600 °C, respectively).

Table 1	The ketalization of cyclohexanone and 1,2-ethanediol to cyclohexanone ethylene ketal	

Entry	Molar ratio ethanediol: cyclohexanone: catalyst	Solvent	Yield	Ref.
1	2000 : 2000 : 1	Cyclohexane	96%	This work
2	900 : 900 : 1	Toluene	~96%	7
3	84.5 : 65 : 1	Toluene	69%	22

Furthermore, the TGA curve and FTIR spectra provide evidence that the Brønsted acidity sites of TiP nanospheres are still stable even after calcination at 400 °C (see Fig. S3 and S4†). The thermogravimetry curve gives a total weight loss of *ca.* 22.4% recorded from room temperature to 1000 °C. The first step before 250 °C in the TGA curve is related to the loss of free adsorptive water, crystal water and hydrogen of AOT which was proved by NMR analysis. The next step from 250 to 350 °C corresponds to the partial release of structural water from the condensation of P–OH groups and loss of carbon of AOT based on the white sample obtained at 350 °C. FTIR spectra of the TiP nanospheres without and with adsorbed pyridine as probe are shown in Fig. S4.† Two bands at 1540 cm⁻¹ and 1490 cm⁻¹ indicated that Brønsted acid sites are present on the surface of the TiP nanoparticles to react with pyridine.²¹

Based on the above discussion, we can draw conclusions concerning the formation mechanism of multicomponent TiP nanospheres. The stable $NaTi_2(PO_4)_3$ crystal was first obtained after the addition of titanium precursors, owing to its poor solubility. Then, an amorphous $Ti(HPO_4)_2$ phase starts to grow with $NaTi_2(PO_4)_3$ as crystal seeds using the acidifying surfactant AOT as template to form core–shell structure TiP nanospheres. Although the core–shell structure is difficult to distinguish due to the closely related components, we could detect the cores from the solution with faint turbidity at the early stage and the core–shell-like structure by heating up to 600 °C (see Fig. S5†).

The stable core-shell TiP nanospheres may find many potential applications as a solid Brønsted acid catalyst due to the open framework with uniform distribution and good dispersion in polar solutions. We used TiP nanospheres as catalyst to catalyze the ketalization of cyclohexanone and 1,2-ethanediol to cyclohexanone ethylene ketal, an important reaction in organic synthesis.^{22,23} The results are shown in Table 1. The molar ratio of cyclohexanone to TiP nanocatalyst (based on Ti atom) was 2000: 1, and the yield could reach 96% in 3 h in cyclohexane at refluxing temperature. This activity is much higher compared to the one reported in ref. 22, which demonstrates a ketal yield of 69% at a cyclohexanone to catalyst molar ratio of 65:1, and the one reported in ref. 7, which shows a similar yield with a lower reactant/catalyst molar ratio of 900:1 in toluene at refluxing temperature. The nanocatalyst also displays very high stability; no obvious decay in catalytic activity was observed when the catalyst was recycled five times. Moreover, as shown in Fig. S6,† the TiP nanocatalyst has very good dispersion in the polar phase and TiP nanocatalyst could precipitate on the bottom of the reactor after the reaction. Therefore, the product could be directly taken out and the recycling of TiP nanocatalyst is very easy without the use of any other process. To our knowledge, it shows the best catalytic activity among all the reported TiP catalysts.

In conclusion, we have synthesized uniform multicomponent TiP nanospheres by a facile approach. The open framework nanospheres with orderly open gradient nanopores have uniform distribution and good dispersion together with a strong acidic surface and large surface area even after high temperature treatment. Moreover, as a solid Brønsted acid, the TiP nanocatalyst has proved to be an extremely active, selective, and stable catalyst for ketalization reactions.

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Notes and references

- J. M. Thomas, O. Terasaki, P. L. Gai, W. Z. Zhou and J. Gonzalez-Calbet, Acc. Chem. Res., 2001, 34, 583–594.
- 2 D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, **102**, 3615–3640.
- 3 G. J. D. Soler-illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093–4138.
- 4 H. O. Pastore, S. Coluccia and L. Marchese, Annu. Rev. Mater. Res., 2005, 35, 351–395.
- 5 Z. Zhang, Y. Han, F.-S. Xiao, S. Qiu, L. Zhu, R. Wang, Y. Yu, Z. Zhang, B. Zou, Y. Wang, H. Sun, D. Zhao and Y. Wei, *J. Am. Chem. Soc.*, 2001, **123**, 5014–5021.
- 6 S. M. Patel, U. V. Chudasama and P. A. Ganeshpure, *React. Kinet. Catal. Lett.*, 2002, **76**, 317–325.
- 7 J. H. Liu, J. L. Zhang, S. Q. Cheng, Z. M. Liu and B. X. Han, Small, 2008, 4, 1976–1979.
- 8 S. M. Patel, U. V. Chudasama and P. A. Ganeshpure, *Green Chem.*, 2001, 3, 143–145.
- 9 S. Sebti, M. Zahouily, H. B. Lazrek, J. A. Mayoral and D. J. Macquarrie, *Curr. Org. Chem.*, 2008, **12**, 203–232.
- 10 A. Clearfield and D. S. Thakur, Appl. Catal., 1986, 26, 1-26.
- 11 A. Bhaumik and S. Inagaki, J. Am. Chem. Soc., 2001, 123, 691-696.
- 12 R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja and C. N. R. Rao, *Chem. Rev.*, 2008, **108**, 3549–3655.
- 13 T. Z. Ren, Z. Y. Yuan, A. Azioune, J. J. Pireaux and B. L. Su, Langmuir, 2006, 22, 3886–3894.
- 14 B. Z. Tian, X. Y. Liu, B. Tu, C. Z. Yu, J. Fan, L. M. Wang, S. H. Xie, G. D. Stucky and D. Y. Zhao, *Nat. Mater.*, 2003, 2, 159–163.
- 15 Z. Yin, Y. Sakamoto, J. Yu, S. Sun, O. Terasaki and R. Xu, J. Am. Chem. Soc., 2004, 126, 8882–8883.
- 16 J. Zhang, Z. Ma, J. Jiao, H. Yin, W. Yan, E. W. Hagaman, J. Yu and S. Dai, *Langmuir*, 2009, **25**, 12541–12549.
- 17 W. H. J. Hogarth, S. S. Muir, A. K. Whittaker, J. C. D. da Costa, J. Drennan and G. Q. Lu, *Solid State Ionics*, 2007, **177**, 3389–3394.
- 18 H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, M. Danjyo and M. Tsuhako, J. Mater. Chem., 1997, 7, 1063–1066.
- 19 L. Mafra, F. A. Almeida Paz, J. Rocha, A. Espina, S. A. Khainakov, J. R. Garcia and C. Fernandez, *Chem. Mater.*, 2005, **17**, 6287–6294.
- 20 L. Mafra, J. Rocha, C. Fernandez, G. Castro, S. Garcia-Granda, A. Espina, S. Khainakov and J. Garcia, *Chem. Mater.*, 2008, 20, 3944–3953.
- 21 G. Zerbi, B. Crawford, Jr. and J. Overend, J. Chem. Phys., 1963, 38, 127–133.
- 22 S. M. Patel, U. V. Chudasama and P. A. Ganeshpure, J. Mol. Catal. A: Chem., 2003, 194, 267–271.
- 23 T. W. G. Peter and G. M. Wuts, in *Greene's Protective Groups in Organic Synthesis (Fourth Edition)*, Wiley, Hoboken, NJ, 2006, pp. 1–15.