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# Synthesis of orderly nanoporous aluminophosphate and zirconium phosphate materials and their catalytic applications†

Peta Sreenivasulu,[ab] Nagabhatla Viswanadham,*[ab] Trymbkesh Sharma[b] and B. Sreedhar[c]

**Amorphous alumino phosphate (AP) and zirconium phosphate (ZP) materials possessing an ordered nanoporosity have been successfully synthesized by a hydrothermal method using a P123 block co-polymer as the structure directing agent. The materials exhibited excellent catalytic activity towards selective alkylation of phenol with cyclohexanol, where AP showed as high as 100% selectivity to produce the industrially important O-alkylation product, while the corresponding ZP selectively produced a C-alkylation product (93% selectivity).**

Porosity is an important feature of materials that plays a vital role in facilitating molecular level interactions of reactants with the active sites and governs their suitability for various applications. Nano-pores, referring to the pores of nanometer range, are recently gaining importance due to their suitability for accommodating bulky molecular transformations. Porous materials should have a narrow pore size distribution which is critical for size-specific applications and a readily tunable pore size allowing flexibility for host–guest interactions and the materials should possess high thermal, chemical and mechanical stabilities, with high surface area and large pore volume.[1] The materials should also have appropriate particle size and morphology.

The ordered framework structures of crystalline aluminosilicate and aluminophosphate materials possessing a uniform (narrow) pore size distribution have been successfully applied for size-specific adsorption, molecular sieving, host–guest chemistry and shape-selective catalysis.[2–6] However, the pore size in such crystalline materials (zeolites) is limited to ~1.5 nm thus excluding size specific processes involving large molecules such as heavy oil conversion in petroleum refining, macromolecule transformations in drug and fine chemical applications, separation processes and for support applications to host large molecules. Further, the narrow pores in such materials also cause severe mass transfer limitations. Here, the amorphous materials provide alternate solution for creation of large size pores (nano-pores > 2 nm) but, obtaining ordered nano-pores in amorphous materials is critical yet important in catalysis and organic synthesis.

Metal phosphates are one of such important materials that need to be addressed for the creation of nano-pores as the applications of many open-framework and layered metal phosphates with varied compositions and properties have been constrained by the lack of large surface areas and the dominance of small pores or interlayer spaces.[7–10] Two synthesis approaches are reported in the literature for these materials. The first approach involves the direct synthesis of nano-porous metal phosphates *via* surfactant templating,[11–19] but the material obtained in this method suffers from the drawbacks of lower surface area and pore volume essential for catalytic applications. The second approach involves the dispersion of metal phosphate guest on nano-porous silica host (possessing large surface areas and ordered nanopores).[20–22] However, it is difficult to finely control the guest–host interaction to obtain homogenous composition and structure *via* wetness impregnation in this method. Though the synthesis of zirconium phosphates by using a P123 block copolymer has been reported, most of the methods involve complicated procedures and longer synthesis times are required to obtain the material.[23,24] These deficiencies prompted us to develop methodologies for the synthesis of metal phosphates with large surface areas and large pores which were successfully explored for the industrially important alkylation of phenol with cyclohexanol. Further, the nature of metal (Al or Zr) is observed to influence the selective alkylation at the oxygen or the carbon atom of the phenol group to produce the desired product.

Herein we report a simple method for the synthesis of zirconium phosphate and alumino phosphate materials by using a P123 block copolymer as an organic template. The typical synthesis method involves the admixing of 6.102 g of P123, 2.12 g of 1 N HCl, 12.21 g of ammoniumdihydrogenphosphate, 75 g of methanol followed by stirring at 60 °C for 2 h until the formation of a clear solution (mixture A). Similarly 28.26 g of zirconium acetylacetonate and 75 g of methanol were admixed

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[a] *AcSIR-Indian Institute of Petroleum, Dehradun, India*
[b] *Catalysis and Conversion Processes Division, Indian Institute of Petroleum, Council of Scientific and Industrial Research, Dehradun-248005, India. E-mail: nvish@iip.res.in; Fax: +91-135-2525702; Tel: +91-135-2525856*
[c] *CSIR-Indian Institute of Chemical Technology, India. E-mail: sreedharb@iict.res.in*

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and heated at 45 °C under stirring for obtaining a clear solution (mixture B). Then mixture A was added slowly to mixture B with continuous stirring (for 30 minutes) to form a precipitate. The resultant mixture was treated inside the Teflon-lined autoclave at 150 °C for 24 h. At the end of the treatment, the compound was washed and collected by filtration, dried and calcined at 500 °C for 5 h. The same procedure is followed for the synthesis of aluminophosphate with the only difference being the use of aluminoisopropoxide in place of zirconium acetylacetonate. The resultant materials are denoted as ZP (zirconium phosphate) and AP (aluminophosphate) respectively.

The presence of Al, Zr, P and O samples was confirmed from EDX analysis (ESI,† Fig. S1). Both AP and ZP samples exhibited similar weight loss patterns in TGA (ESI,† Fig. S2), where a major weight loss of ~17–26 wt% was related to the degradation of P123-polymer was observed. The minor weight losses of 1.8–4.3 wt% were also observed at higher temperature range of 400–500 °C in these samples, which indicates the continuous dehydrogenation and carbonization processes of the polymer species. These results indicate that the copolymer templates can be decomposed by calcination at 500 °C for 5 h under $N_2$.[25]

The low-angle XRD patterns (ESI,† Fig. S3) of AP and ZP samples reveal the presence of mesopores in these materials.[26] A wide angle XRD of AP and ZP shows that both the samples are amorphous in nature (ESI,† Fig. S4). The SEM (ESI,† Fig. S5) and TEM images (Fig. 1) reveal the porous nature of the samples. The enlarged portion given in Fig. 1C and D indicates the uniformly distributed pores. Such a porous material is expected to exhibit high surface area and porosity. The porosity of the AP and ZP samples measured by $N_2$ adsorption–desorption measurements (Fig. 2) further confirms the presence of mesopores. The adsorption–desorption isotherm also represents mixed types of isotherms (combination of types I, II and IV). The isotherm indicates the occurrence of well-defined capillary condensation at a relative pressure ($P/P_o$) of 0.5–1.0. The BJH pore size distribution curve of AP and ZP samples (Fig. 2, inset) reveals the presence of mesopores. However, the shape of isotherms is different for two samples this may be due to the difference in the interaction of the chemical ingredients and the distribution of the organic template with Al and Zr. This is also reflected in the difference in the BET surface area (370 $m^2$ $g^{-1}$ and 180 $m^2$ $g^{-1}$) and pore volume (1.17 $cm^3$ $g^{-1}$ and 0.51 $cm^3$ $g^{-1}$) of the AP and ZP samples (Table 1). The relatively low surface area and pore volume observed in ZP can be ascribed to the involvement of heavy metal Zr and the higher density of the material. Both the samples exhibited similar BJH pore size distribution patterns with the majority of pores having a diameter of 5 nm (peak maxima in Fig. 3) revealing the formation of ordered nano-size pores in these two amorphous materials.

The acidity patterns measured by TPD (Fig. 3) indicate the presence of two $NH_3$ desorption peaks in both the samples: one

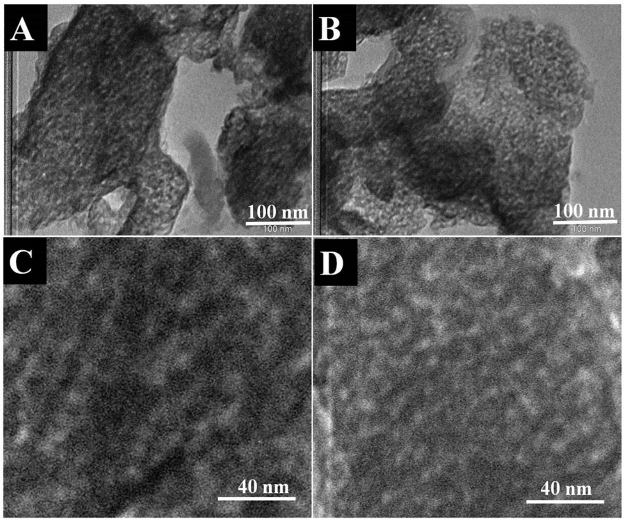

Fig. 1 A, C and B, D are TEM images of AP, and ZP samples respectively.

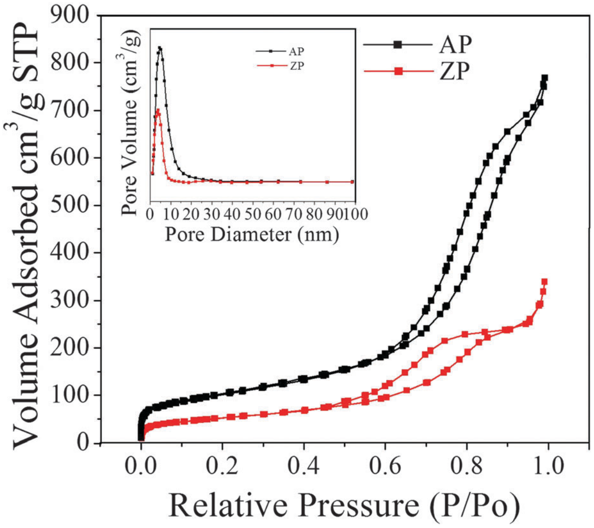

Fig. 2 $N_2$ adsorption–desorption isotherm, and BJH pore size distribution of AP and ZP materials (inset).

Table 1 Textual properties of AP and ZP samples

| Samples | BET surface area ($m^2$ $g^{-1}$) | Total pore volume ($cm^3$ $g^{-1}$) | Mean pore diameter (nm) |
|---|---|---|---|
| AP | 370 | 1.17 | 12.68 |
| ZP | 188 | 0.51 | 10.92 |

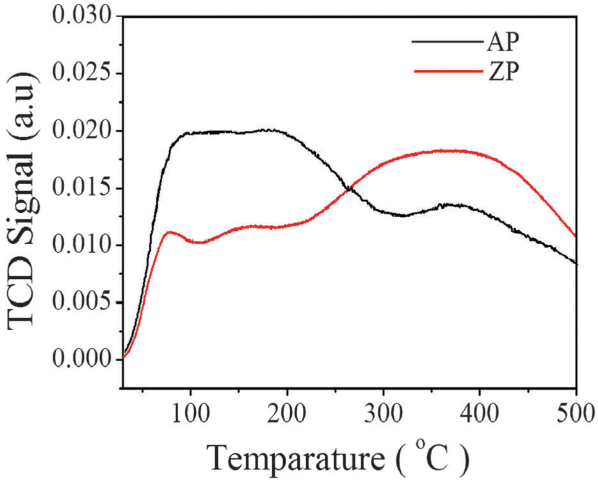

Fig. 3 TPD spectra of the AP and ZP samples.

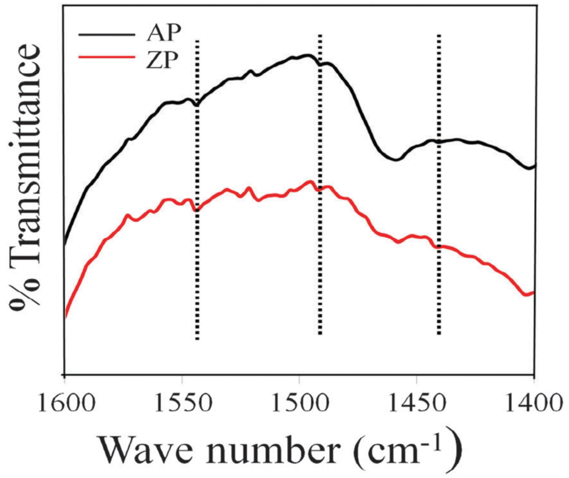

Fig. 4 Pyridine FT-IR XRD of the AP and ZP samples.

broad peak centered at 150 °C and the other around 400 °C representing the weak and strong acid sites respectively. The intensity of the strong acidity peak is relatively higher in the case of ZP, which indicates the creation of strong acid sites *via* the interaction of Zr with P in this material. The nature of acidity is further characterized using Pyridine FT-IR spectroscopy (Fig. 4). Usually, the IR bands appearing at 1540–1548 $\text{cm}^{-1}$ and 1445–1460 $\text{cm}^{-1}$ are related to Brønsted (B) and Lewis (L) acid sites respectively. The IR patterns given in Fig. 4 clearly indicate the presence of both Brønsted and Lewis acid sites in both AP and ZP samples. However, a higher intensity of both Brønsted (at ~1540) and Lewis (~1445) acid sites was observed in the sample ZP when compared to those in AP. A band at ~1490 related to the combination of both Brønsted and Lewis acid sites is also observed in both the samples.[27]

Catalytic alkylation of substituted phenols with cyclohexanol is one of the most important industrial organic reactions.[28] These reactions yield both O- and C-alkylated products having commercial utility. The O-alkylated products are promising perfumery compounds,[29] whereas the C-alkylated products are used as important intermediates in the preparation of dyestuffs, drugs, printing inks, wire enamels, rubber chemicals, petroleum additives, polymer additives, resins and so on.[30] Hence, the selective production of each alkylated product is quite challenging in these reaction processes. The concept of green chemistry and its applications in synthetic organic chemistry has been emerging as major route for the development of clean chemical synthesis. A green chemical process for sustainable development always involves considerations such as the use of cost-effective catalysts without any additives and employing a solvent-free system.[31] In alkylation of phenol with cyclohexanol very few catalysts have been used, such as the cation-exchange resin KU-2, H-zeolite and other conventional Lewis and Brønsted acid catalysts.[32] But these catalysts produce many side products, and the process is time consuming and consumes a large amount of solvent that gets wasted. Hence, the development of an environmentally benign catalyst that works in solvent-free alkylation, yet exhibits efficient activity is a challenging task for modern organic synthesis. The AP and ZP samples possessing nanoporosity along with acidity are expected to exhibit promising catalytic activity towards this reaction. In the present study we have conducted reaction studies on these two nanoporous materials for the selective alkylation of phenol with cyclohexanol (ESI†). The influence of the reaction temperature and reaction time was studied to understand the catalyst performance. By varying the reaction temperature from 50 to 150 °C, a gradual improvement in conversion of cyclohexanol (48 to 68%) and selectivity of O-alkylated product (100%) is observed for the AP sample (Table 2, entries 1 to 3). The ZP sample also exhibited a similar trend in conversion of cyclohexanol (82 to 100%) and selectivity of the C-alkylated product (88 to 93%) for a constant reaction time of 4 h (Table 2, entries 1 to 3). However, further increase in the reaction temperature (175 °C) did not cause any significant effect on the conversion values of both the catalysts (Table 2, entries 4 for AP and 4 for ZP). By varying the reaction time from 1 to 4 h, a gradual improvement in conversion of cyclohexanol (39 to 68%) and selectivity of O-alkylated product (100%) is

Table 2 Performance of catalysts in phenol alkylation reaction

| | | | | | Product selectivity (%) | |
|---|---|---|---|---|---|---|
| Entry | Catalyst | Temperature (°C) | Time (h) | Cyclohexanol conversion (%) | O-alkylation | C-alkylation |
| 1 | AP | 50 | 4 | 48 | 100 | — |
| 2 | | 100 | 4 | 56 | 100 | — |
| 3 | | 150 | 4 | 68 | 100 | — |
| 4 | | 175 | 4 | 66 | 100 | — |
| 5 | | 150 | 1 | 39 | 100 | — |
| 6 | | 150 | 2 | 47 | 100 | — |
| 7 | | 150 | 3 | 53 | 100 | — |
| 8 | | 150 | 6 | 69 | 100 | — |
| 1 | ZP | 50 | 4 | 82 | 12 | 88 |
| 2 | | 100 | 4 | 87 | 9 | 91 |
| 3 | | 150 | 4 | 100 | 7 | 93 |
| 4 | | 175 | 4 | 99 | 6 | 94 |
| 5 | | 150 | 1 | 62 | 20 | 80 |
| 6 | | 150 | 2 | 73 | 14 | 86 |
| 7 | | 150 | 3 | 87 | 11 | 89 |
| 8 | | 150 | 6 | 99 | 6 | 94 |

Phenol = 1 mole, cyclohexanol = 1 mole, catalyst = 0.5 g.

observed for the AP sample (Table 2, entries 5 to 7 and 3). The ZP sample also exhibited the same trend in conversion of cyclohexanol (62 to 100%) and selectivity of C-alkylated product (80 to 93%) at a constant reaction temperature of 150 °C (Table 2, entries 5 to 7 and 3). However, further increase in reaction time (6) did not cause any significant effect on the conversion values of both the catalysts (Table 2, entries 8 for AP and 8 for ZP). Overall, the AP/ZP catalysts of the present study exhibited maximum catalytic activity at 150 °C within a short reaction time of 4 h reveals the promising catalytic activity of the samples.

The AP catalyst exhibited as high as 100% selectivity (Table 2) towards the O-alkylation product at 68% conversion values. At similar reaction conditions, the ZP exhibited as high as 100% conversion with shifting of selectivity towards C-alkylation (93% selective) from the O-alkylation product. Earlier alkylation studies on other types of catalysts such as zeolites indicated that the large pore size of catalysts is responsible for ring alkylation whereas a narrow pore size favors O-alkylation.[33,34] Prins *et al.*[35] mentioned that the alkylation mainly occurred in the mesoporous parts of zeolites due to the limitation for diffusion of bulky molecules in the narrow pores. Moreover, the selectivity towards a particular product was mainly directed by the acidity of the catalyst system used.[36] Based on these reports we can deduce that both mesoporosity and external acid sites of catalysts play an important role in activity and selectivity in such chemo-selective alkylation reactions. The higher conversion values and C-alkylation activity of the ZP catalyst of the present study can be ascribed to its higher acidity in terms of both Brønsted and Lewis acid sites (since the porosity of ZP is comparable with that of AP). The studies, for the first time, indicate the potential applications of these materials for selective O-alkylation (AP) and C-alkylation (ZP) reactions. A reference experiment was also conducted in the absence of the catalyst, using only phenol and cyclohexanol, where no reaction was observed to proceed, which confirms the catalytic role of AP/ZP materials. The AP/ZP materials of the present study exhibited superior performance over those reported in the literature (ESI,† Table S1).

In summary, the present study provides a simple and novel method for the synthesis of ordered nanoporous aluminophosphate and zirconiumphosphate materials possessing promising catalytic activity towards industrially important selective alkylation of phenol for the efficient production of C-alkylation and O-alkylation products. Further, the materials show their reusability with an excellent catalytic performance even after five reaction cycles (ESI,† Table S2). The subject opens up a new property of the nanoporous aluminophosphate and zirconiumphosphate materials as suitable catalysts for selective alkylation reactions and has scope for improvement of the catalytic activity through the optimization of the synthesis procedure of nanoporous aluminophosphate and zirconiumphosphate for expanding their applications to other selective alkylation reactions.

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## Notes and reference

1 (*a*) P. Behrens, *Adv. Mater.*, 1993, **5**, 127; (*b*) T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.
2 D. W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons, New York, London, 1974, p. 784.
3 A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Wiley & Sons, New York, London, 1988, p. 164.
4 W. F. Holderich, M. Hesse and F. Naumann, *Angew. Chem., Int. Ed.*, 1988, **27**, 226.
5 *Advanced Zeolite Science and Applications, Studies in Surface Science and Catalysis*, ed. J. C. Jansen, M. Söcker, H. G. Karge and J. Weitkamp, Elsevier, Amsterdam, vol. 85, 1994, p. 708.
6 (*a*) A. Corma, *Chem. Rev.*, 1995, **95**, 559; (*b*) A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
7 H. E. Katz, G. Scheller, T. M. Putvinski, M. L. Schilling, W. Wilson and C. E. D. Chidsey, *Science*, 1991, **254**, 1485.
8 C. Guang, H. G. Hong and T. E. Mallouk, *Acc. Chem. Res.*, 1992, **25**, 420.
9 (*a*) G. Freiman, P. Barboux, J. Perriere and K. Giannakopoulos, *Chem. Mater.*, 2007, **19**, 5862; (*b*) D. W. Jing and L. J. Guo, *J. Phys. Chem. C*, 2007, **111**, 13437; (*c*) D. P. Das and K. M. Parida, *Catal. Surv. Asia*, 2008, **12**, 203.
10 (*a*) D. M. Poojary, B. Shpeizer and A. Clearfield, *J. Chem. Soc., Dalton Trans.*, 1995, 111; (*b*) S. Bruque, M. A. G. Aranda, E. R. Losilla, P. O. Pastor and P. M. Torres, *Inorg. Chem.*, 1995, **34**, 893; (*c*) S. Ekambaram and S. C Sevov, *Angew. Chem., Int. Ed.*, 1999, **38**, 372; (*d*) J. H. Yu and R. R. Xu, *Chem. Soc. Rev.*, 2006, **35**, 593.
11 J. J. Jimenez, P. M. Torres, P. O. Pastor, E. R. Castellon, A. J. Lopez, D. J. Jones and J. Roziere, *Adv. Mater.*, 1998, **10**, 812.
12 D. J. Jones, G. Aptel, M. Brandhorst, M. Jacquin, J. J. Jimenez, A. J. Lopez, P. M. Torres, I. Piwonski, E. R. Castellon, J. Zajac and J. Roziere, *J. Mater. Chem.*, 2000, **10**, 1957.
13 X. F. Guo, W. P. Ding, X. G. Wang and Q. J. Yan, *Chem. Commun.*, 2001, 709.
14 A. Bhaumik and S. Inagaki, *J. Am. Chem. Soc.*, 2001, **123**, 691.
15 S. D. Shen, B. Z. Tian, C. Z. Yu, S. H. Xie, Z. D. Zhang, B. Tu and D. Y. Zhao, *Chem. Mater.*, 2003, **15**, 4046.
16 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.
17 J. E. Haskouri, C. Guillem, J. Latorre, A. Beltran, D. Beltran and P. Amoros, *Chem. Mater.*, 2004, **16**, 4359.
18 M. P. Kapoor, S. Inagaki and H. Yoshida, *J. Phys. Chem. B*, 2005, **109**, 9231.
19 (*a*) D. H. Yu, C. Wu, Y. Kong, N. H. Xue, X. F. Guo and W. P. Ding, *J. Phys. Chem. C*, 2007, **111**, 14394; (*b*) M. Anabia, M. K. Rofouel and S. W. Husain, *Chin. J. Chem.*, 2006, **24**, 1026.
20 Y. Wang, X. X. Wang, Z. Su, Q. Guo, Q. H. Tang, Q. H. Zhang and H. L. Wan, *Catal. Today*, 2004, **93–95**, 155.
21 X. K. Li, W. H. Ji, J. Zhao, Z. Zhang and C. T. Au, *Appl. Catal., A*, 2006, **306**, 8.
22 X. K. Li, W. H. Ji, J. Zhao, Z. B. Zhang and C. T. Au, *J. Catal.*, 2006, **238**, 232.
23 W. H. J. Hogarth, J. C. D. Costa, J. Drennan and G. Q. (Max) Lu, *J. Mater. Chem.*, 2005, **15**, 754.
24 Y. Nishiyama, S. Tanaka, H. W. Hillhouse, N. Nishiyama, Y. Egashira and K. Ueyama, *Langmuir*, 2006, **22**, 9469.
25 Y. Yan, F. Zhang, Y. Meng, B. Tu and D. Zhao, *Chem. Commun.*, 2007, 2867.
26 Z. Niu, S. Kabisatpathy, J. He, L. A. Lee, J. Rong, L. Yang, G. Sikha, B. N. Popov, T. S. Emrick, T. P. Russell and Q. Wang, *Nano Res.*, 2009, **2**, 474.
27 N. Pethan Rajan, G. S. Rao, V. Pavankumar and K. V. R. Chary, *Catal. Sci. Technol.*, 2014, **4**, 81.
28 R. Anand, K. U. Gore and B. S. Rao, *Catal. Lett.*, 2002, **81**, 33.
29 A. Chakrabarti and M. M. Sharma, *React. Polym.*, 1992, **17**, 331.
30 G. D. Yadav and G. S. Pathre, *Ind. Eng. Chem. Res.*, 2007, **46**, 3119.
31 Y. Zhao, J. Li, C. Li, K. Yin, D. Ye and X. Ji, *Green Chem.*, 2010, **12**, 1370.
32 A. M. Ravikovich, *J. Chem. Soc., Chem. Commun.*, 1991, **3**, 9–64.
33 G. D. Yadav and P. Kumar, *Appl. Catal., A*, 2005, **286**, 61.
34 R. Anand, T. Daniel, R. J. Lahoti, K. V. Srinivasan and B. S. Rao, *Catal. Lett.*, 2002, **81**, 241.
35 X. Li, R. Prins and J. A. Bokhoven, *J. Catal.*, 2009, **262**, 257.
36 N. Candu, M. Florea, S. M. Coman and V. I. Parvulescu, *Appl. Catal., A*, 2011, **393**, 206.