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Increasing the H^+ exchange capacity of porous titanium phosphonate materials by protecting defective P–OH groups†

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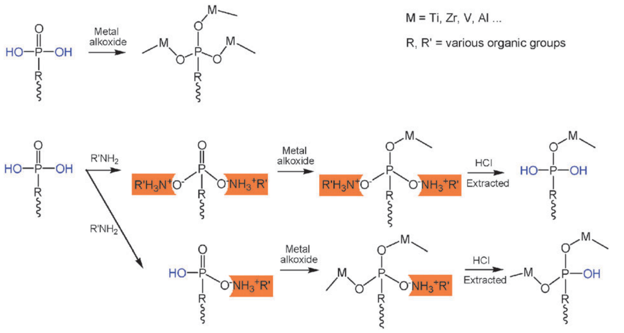
Hierarchically macro-/mesoporous titanium phosphonates with enlarged H^+ exchange capacity were synthesized in the presence of a series of alkyl amines that acted as protective groups for the defective P–OH, which were used as promising solid acid catalysts to replace conventional liquid acid catalysts and acidic resins in some acid-catalytic reactions.

Mesoporous metal phosphate and phosphonate materials have become new potential candidates for ion exchange and acid catalysis due to their advantages of accessible ion-exchange capacities,[1,2] well-defined pore structures with large specific surface areas and some hierarchical micro-architectures,[3] and high thermal stability,[4] which are superior to the traditional polymer ion-exchange resins. However, the H^+ exchange capacity of metal phosphates and phosphonates was usually limited, because the H^+ exchange of these materials is due to the defective P–OH groups in the resultant solids,[5] while the condensation between P–OH and metal ions during the preparation process often results in the extensive formation of P–O–Me (Me = Ti, Zr, V, Al, *etc.*) bonding mode instead of defective P–OH.[6] Thus it is urgent from a technical viewpoint to develop an efficient way to increase the defective P–OH concentration in metal phosphates and phosphonates for the improvement of the H^+ exchange capacity, namely, the acid content.

Metal phosphonates stand for an important family of organic–inorganic hybrid materials, which have recently attracted much attention because of the combination of properties due to both inorganic and organic moieties.[7] The integration of bridging organic groups into the inorganic component framework could not only adjust the hydrophilic/hydrophobic nature of the pore surface but also introduce functional sites into the hybrid network.[8] Therefore, the host–guest selectivity between the organophosphonate groups and the substrates, which hardly exists in purely inorganic metal phosphate materials, and the inherent acidity from P–OH defects have determined the metal phosphonate materials to be outstanding acid catalysts.[9] In this contribution, hierarchically macro-/mesoporous titanium phosphonate materials were synthesized by a one-pot template-free method, constructed from diethylenetriamine penta(methylene phosphonic acid) (DTPMPA, Scheme S2, ESI†). The preparation was carried out in the presence of a series of alkyl amines with different concentrations, acting as protective groups during the condensation process to increase the defective P–OH content (Scheme 1). The designed porous titanium phosphonates with large H^+ exchange capacity were further used as acid catalysts in the synthesis of methyl-2,3-*o*-isopropylidene-β-D-ribofuranoside, the key intermediate for the preparation of several important nucleosides, which exhibit a variety of biological functions.[10]

The condensation between DTPMPA and tetrabutyl titanate was performed in the presence of *n*-propylamine, *n*-butylamine and *n*-pentylamine with different concentrations (ESI†), and the obtained porous titanium phosphonates were denoted as TiPPh-amine. In comparison, the sample synthesized in the absence of alkyl amine was denoted as TiPPh-non. As shown in Scheme 1, the reversible reaction between alkyl amines and P–OH groups could greatly increase the defective P–OH in the resultant solids, which could be proved when appropriate amounts of *n*-butylamine (amine/DTPMPA molar ratio of 0.3) were added into the reaction system with increase of P/Ti molar ratios (Fig. 1, left). In the absence of amines, although the P/Ti molar ratio in the obtained solids increased by increasing the added P/Ti ratio in raw materials, due to the limit of coordination ability of Ti^{4+} ions with phosphonic acids,[4] the P/Ti ratio reached a plateau of 1.35–1.51 when the added P/Ti ratio was larger than 1.75.



Scheme 1 Alkyl amine-assisted preparation of titanium phosphonates.

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† Electronic supplementary information (ESI) available: Experimental details, N_2 sorption, XRD, FT-IR spectra, Hammett acidities and recycle profiles of the catalysts. See DOI: 10.1039/c1cc11583a

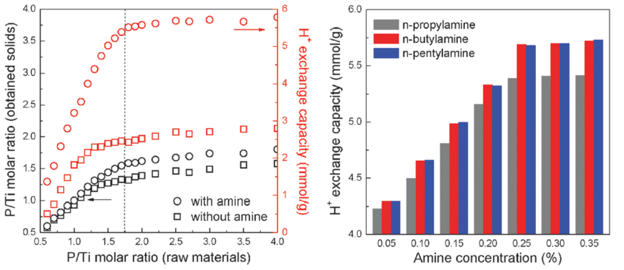

Fig. 1 P/Ti molar ratios in the obtained solids and H^+ exchange capacities *versus* added P/Ti ratios in the raw materials (*n*-butylamine/DTPMPA molar ratio of 0.3) (left). H^+ exchange capacities of titanium phosphonates synthesized in the presence of various alkyl amines with different concentrations (added P/Ti molar ratio of 2.5) (right).

In the presence of amines, the P/Ti ratio of obtained solids also exhibited a sharp initial rise, and finally reached a plateau of 1.59–1.80, which was higher than that without amines added. Correspondingly, a similar tendency could be observed for H^+ exchange capacity of the synthesized materials. The highest H^+ exchange capacities could be confirmed as 2.44–2.79 and 5.51–5.80 mmol g^{-1} for the samples synthesized without and with *n*-butylamine assistance, respectively, which demonstrated that the presence of alkyl amines in the reaction system could efficiently increase the P/Ti molar ratio, more importantly the H^+ exchange capacity, of resultant materials. This could be explained by the fact that the alkyl amines first partially occupied P–OH sites by acid–base reactions, followed by the condensation between the added alkoxides and residual P–OH and P=O groups (Scheme 1). And the extraction with HCl would finally release P–OH defects of the resultant solids, leading to the high H^+ exchange capacity and acid content. However, the enhancement effect was hardly detected when $NH_3{\cdot}H_2O$ was used instead of alkyl amines, probably because NH_3 was too volatile to form relatively stable bonding with P–OH in the competitive reaction with alkoxides. The observed H^+ exchange capacities of 5.51–5.80 mmol g^{-1} in resultant samples are much larger than those in the previously reported titanium phosphates[5] (1.7–3.4 mmol g^{-1}) and titanium phosphonates[2] (3.93 mmol g^{-1}). Furthermore, when the added P/Ti molar ratio was fixed at 2.5, which was within the plateau range mentioned above, and various amines were employed into the system with different concentrations, it could be seen in Fig. 1 (right) that the H^+ exchange capacities increased when the amine concentration (amino/DTPMPA molar ratio) is in the range from 0.05 to 0.25, and kept stable from 0.25 to 0.35. The enhancement effect provided by *n*-butylamine and *n*-pentylamine was approximate but greater than that by *n*-propylamine. Thus titanium phosphonate material synthesized with an added P/Ti ratio of 2.5 and *n*-butylamine/DTPMPA ratio of 0.3 (TiPPh-butylamine) was chosen here for the following discussions.

FT-IR and MAS NMR measurements were employed to further confirm the functions of alkyl amine assistance. The FT-IR spectra of TiPPh-butylamine and TiPPh-non are shown in Fig. 2. The strong broad band at 3400 cm^{-1} and the sharp band at 1642 cm^{-1} correspond to the surface-adsorbed water and hydroxyl groups. The strong band at 1050 cm^{-1} is due to phosphonate P–O···Ti stretching vibrations.[4,6] The overlapped bands at 1462 and 1433 cm^{-1} are assigned as the C–H bending in $–CH_2–$ groups and the P–C stretching vibrations, respectively. The small bands at 1323 cm^{-1} could be attributed to C–N stretching.[4] No bands at around 1380 or 1137 cm^{-1} were found for phosphoryl (P=O) frequency, indicating the full condensation between phosphoryl and Ti atoms.[11] In addition, several bands around 2900–3000 cm^{-1} are assigned to the C–H stretching modes. The band at 970 cm^{-1} assigned to P–OH stretching vibrations[11,12] was not observed in TiPPh-non (Fig. 2a), showing the low content of defective P–OH groups in TiPPh-non, which was enveloped in the strong band at 1050 cm^{-1} (P–O···Ti). A shoulder peak is observed at around 970 cm^{-1} for the as-synthesized TiPPh-butylamine sample before HCl extraction (Fig. 2b), but transformed into a newborn peak after HCl extraction (Fig. 2c), indicating a large amount of P–OH defects.[11,12] Noticeably, the increase of C–H stretching strength at 2900–3000 cm^{-1} and C–N stretching strength at 1323 cm^{-1}, and the existence of N–H bending vibrations in $NH_2–$ groups at 845 cm^{-1} (Fig. 2b) also confirmed the participation of alkyl amines.[13] Correspondingly, the ^{31}P MAS NMR spectrum of TiPPh-non shows one broad signal around 21.5 ppm (Fig. 2a), which is in the area characteristic of phosphonates,[6,8] while the spectrum of TiPPh-butylamine (Fig. 2c) shows two resonance signals of the phosphorus nuclei at 21.3 and 29.2 ppm, which could be assigned to P atoms in $–RPO_3Ti_3$ and in the mixture of $–RPO_3H_2Ti$ and $–RPO_3HTi_2$, respectively.

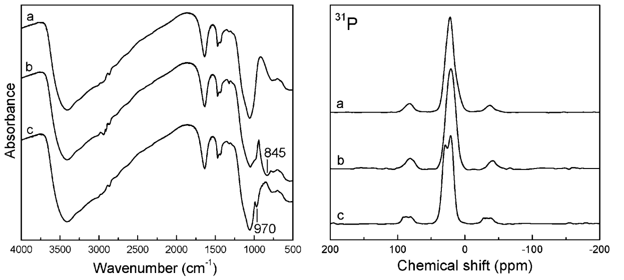

Fig. 2 FT-IR (left) and MAS NMR (right) spectra of (a) titanium phosphonates synthesized without amines, and titanium phosphonates synthesized with *n*-butylamines (b) before and (c) after HCl extraction.

The morphology, pore structure and texture properties of the synthesized TiPPh-amine catalyst were then characterized. SEM images revealed a channel-like macroporous structure with a uniform pore diameter distribution of 500–1000 nm (Fig. 3a). The macrochannels are mainly of one-dimensional orientation, parallel to each other, perforative through almost the entire particle (Fig. 3a, inset). It is revealed by the TEM observation (Fig. 3b) that the walls of the macroporous network are composed of accessible wormhole-like mesopores. The N_2 sorption analysis also indicated the hierarchical porosity with a surface area of 269 m^2 g^{-1}, a pore volume of 0.22 cm^3 g^{-1} and a pore size of around 5.1 nm (Fig. S1a, ESI†).

The large H^+ exchange capacity of titanium phosphonates synthesized with amines assistance could make these materials act as practical acid catalysts potentially useful in many reactions. The condensation reaction of D-ribose with acetone and methanol to produce methyl-2,3-*o*-isopropylidene-β-D-ribofuranoside was chosen herein, which was catalyzed by

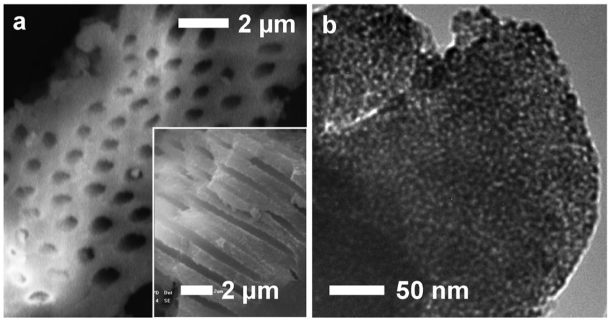

Fig. 3 SEM (a) and TEM (b) images of the TiPPh-butylamine material.

some homogenous catalysts such as H_2SO_4 and HCl (Scheme S1, ESI†).[14] Porous titanium phosphate (TiP-butylamine) was also synthesized with the use of phosphoric acid instead of DTPMPA in the presence of *n*-butylamine. TiPPh-butylamine, TiP-butylamine, TiPPh-non, previously reported ordered mesoporous titanium phosphonates constructed by ethylenediamine tetra(methylene phosphonic acid) (PMTP-1),[4] commercial acidic resin NKC-9 and concentrated HCl (conc. HCl) were all tested for a 3 h reaction (Table 1). A scarce product was obtained when catalyzed by TiPPh-non and PMTP-1 due to their low acid content (2.54 and 2.93 mmol g^{-1}) and acid strength ($H_0 > -8.20$, Table S1, ESI†). However, with the assistance of alkyl amines, both the acid contents of TiPPh-butylamine (5.76 mmol g^{-1}) and TiP-butylamine (5.71 mmol g^{-1}), and the acid strength ($H_0 < -8.20$) were increased, leading to high yields of 48.7 and 42.8% for methyl-2,3-*o*-isopropylidene-β-D-ribofuranoside, respectively. The yields were even higher than that of NKC-9 (33.0%) with the acid content of 4.33 mmol g^{-1}, which could be attributed to the low surface area of NKC-9 (12 m^2 g^{-1}). Thus under the present experimental conditions, the catalytic ability of these solid acids was not only related to the H^+ exchange capacity (acid content) but also to the acid strength. For the solid catalysts with $H_0 > -8.20$ (TiPPh-non, PMTP-1), the condensation reaction shown in Scheme S1 (ESI†) could hardly proceed; for the solid catalysts with $H_0 < -8.20$ (TiPPh-butylamine, TiP-butylamine, NKC-9), the condensation reaction could proceed and the yields were further determined by the acid contents and pore structure (surface area, pore volume, *etc.*) of the materials. It is noticeable that with both catalysts having a similar pore structure, acid content and strength, the organic–inorganic hybrid TiPPh-butylamine catalyst has a higher yield (+5.9%) than the purely inorganic TiP-butylamine catalyst, which might be explained by the strong affinity between the organic motifs in the hybrid network of titanium phosphonates and the substrates.[2,15] The conc. HCl catalyst showed the yield of 26.2% after refluxing for 3 h; but by extending the refluxing time to 18 h, the yield while using the HCl catalyst could be increased to 50%,[14] similar to the yield while using the TiPPh-butylamine catalyst after refluxing for 3 h (48.7%), which indicated the high reaction rate by using phosphonate-based catalysts. After 10-time reuse, the product yield was hardly decreased (Fig. S2, ESI†). Thus the TiPPh-butylamine material was proved to be an efficient acid catalyst with desirable stability and good recyclability, which could replace the conventional acid catalysts like conc. HCl and acidic resins in this reaction shorten the reaction time and overcome disadvantages of homogeneous catalysts such as being difficult to separate and recover and harmful to the environment.

Table 1 Comparison of different acid catalysts

Sample	$S_{BET}{}^{a}$/ m^2 g^{-1}	$V_{pore}{}^{b}$/ cm^3 g^{-1}	$D_{pore}{}^{c}$/ nm	H^+ exchange capacity/mmol g^{-1}	Yield (%)
TiPPh-butylamine	269	0.22	5.1	5.76	48.7
TiPPh-non	242	0.21	5.1	2.54	1.3
TiP-butylamine	281	0.23	5.2	5.71	42.8
PMTP-1[d]	1066	0.83	2.8	2.93	2.2
NKC-9[e]	12	0.02	—	4.33	33.0
Conc. HCl	—	—	—	—	26.2

[a] BET surface area calculated from the linear part of the 10-point BET plot. [b] Single point total pore volume of pores at $P/P_0 = 0.97$. [c] Estimated using the adsorption branch of the isotherm by the BJH method. [d] Periodic mesoporous titanium phosphonate materials (see ref. 4). [e] The commercial acidic resin.

This strategy is supposed to open a new area in the development of outstanding phosphonate-based acid catalysts and ion exchangers by the defect protection method. Only small amounts of alkylamines were necessary instead of other expensive additives, and the facile one-pot preparation process also makes the present acid catalyst practical in some reactions in the chemical industry. Moreover, because the P–OH groups serve as carriers of protons, these materials may also find use as an electrolyte for fuel cells.

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