Mesoporous Zirconium Phosphate-phenylphosphonate and Its Functionalization

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Mesoporous zirconium phosphate-phenylphosphonate has been prepared in the presence of cetyltrimethylammonium bromide as the template. The phenyl groups on the pore wall could be easily sulphonated or brominated to endow the sample with more functionalities.

Metal phosphates and phosphonates are the important catalytic materials owing to their ordered but diversed structure and surface properties. Up to now, a series of papers have been published on the preparation and application of the layered metal phosphates, phosphonates and their hybrids whose surface properties could be controlled through simply functionalizing the organic groups between the layers.[1,2] Recently, the preparation of silica-based mesoporous materials has been well developed for their specialities like the high surface areas and ordered and tunable pore diameters[3] and many efforts have also been made to prepare the mesoporous metal phosphates which might exhibit more advantages over their layered analogues. To date, aluminium phosphate,[4] titanium phosphate,[5] zirconium phosphate,[6] tin phosphate[7] and iron phosphate[8] have been already prepared. However, only until very recently, a few kinds of the hybrid mesoporous metal phosphonates have been reported.[9] These materials might find more interesting catalytic properties after those organic groups in the mesoporous materials were functionalized. Here, we report the synthesis of the mesoporous zirconium phosphate-phenylphosphonate and further introducing the functional groups through sulphonation or bromination reactions on the phenyl groups.

A typical synthesis procedure of the hybrid zirconium phosphate-phenylphosphonate (MZPPh) was as follows: a mixture of phosphorous acid (85 %) and phenylphosphonic acid ($PhPO(OH)_2$) was added to an aqueous solution containing 25 wt% cetyltrimethylammonium bromide (CTAB), and aged for 2 h at room temperature. Then zirconium isopropoxide, ($Zr(OPr\text{-}i)_4$, 70 wt% in isopropanol) was added dropwise under stirring. The molar ratio of the components in the final mixture was 1.0 $Zr(OPr\text{-}i)_4$: 1.8 H_3PO_4: 0.2 $PhPO(OH)_2$: 1.0 CTAB: 61 H_2O. The reaction mixture was vigorously stirred for 3 days at ambient temperature. The product was recovered by centrifugation, washed with ethanol and dried at 80 °C for 12 h. The surfactant in the as-synthesized sample was removed through solvent extraction with the protonated ethanol under refluxing.[6] The introducing of $-SO_3H$ groups was carried out by immersing 0.6 g of the solvent extracted MZPPh into 10 ml of fuming sulphuric acid (150 wt%) at 55 °C and stirred for 15 min. After evaporating the excess SO_3, it was slowly diluted by a large quantity of water in an ice/water bath. The sulphonated product (MZPPh-sul) was centrifugated, washed and dried at 60 °C. The brominating of the sample was also achieved by adding 10 ml of liquid bromine into a mixture of 0.6 g extracted MZPPh and 1.0 g iron powder at 60 °C. The reaction mixture was stirred for 4 h and a large quantity of water was then added. The separation procedure of the brominated sample (MZPPh-bro) was the same as that of the sulphonated sample.

The X-ray diffraction (XRD) pattern of the as-synthesized sample shows one clear diffraction peak at 2θ of ca. 2°, indicating the formation of mesostructure. After extracting the template, the peak can still be identified but obviously broadened (Figure 1a and b). The TEM image of the extracted sample presents a worm-like pore structure with a diameter of ca. 2 nm (Figure 2a). The mesoporosity of MZPPh is also proved by the N_2-adsorption experiment at 77 K. The extracted sample has a relatively high BET surface area of about 343 m^2/g with a pore volume of 0.28 cm^3/g. The mesopore distribution (calculated by the adsorption branch of the isotherm using the BJH model) is shown in Figure 2d with a mean diameter of 1.7 nm, smaller than that of the reported mesoporous zirconium phosphates[6] (2.3 nm). This change was probably caused by the fact that some spaces of the channels have been occupied by the phenyl groups exserted from the pore walls. The incorporation of the phenyl groups is evidently testified by its IR spectrum (Figure 3). Besides the peaks assigned to phosphate, the peaks at 750, 730, and 690 cm^{-1} attributed to the C-H out of plane bending vibrations of the aromatic group of $PhPO(OH)_2$[10,11] are also observed. Furthermore, the entrance of the phenyl groups in mesoporous hybrid samples is also confirmed by the ^{31}P MAS NMR experiment. In addition to the peaks with a maximum at ca. −20.7 ppm, which were assigned to PO_4 units bonded to the Zr atoms,[6] a new signal at ca. −5.0 ppm with the intensity of about 1/9 of that of PO_4 appeared which could be attributed to the phosphorous atoms

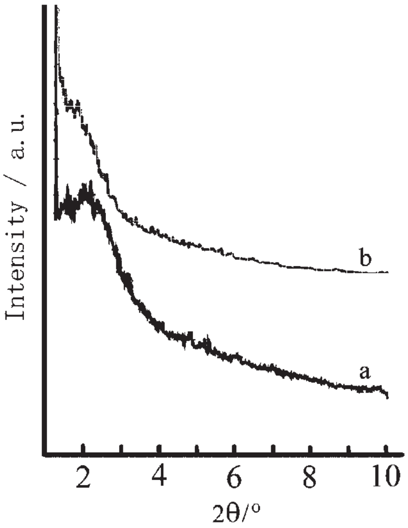

Figure 1. XRD patterns of MZPPh before (a) and after (b) removing the templates.

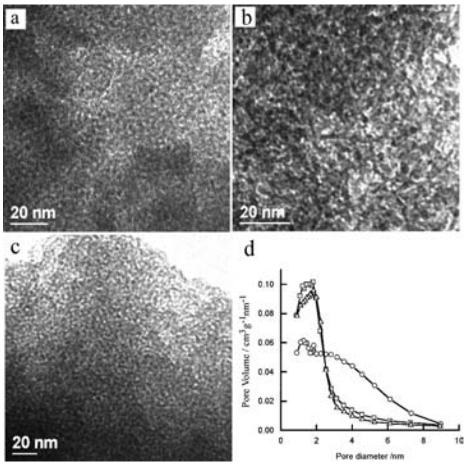

Figure 2. TEM images of (a) MZPPh, (b) MZPPh-sul and (c) MZPPh-bro; (d) mesopore distribution of MZPPh (square), MZPPh-sul (cycle) and MZPPh-bro (triangle), calculated using BJH model from the adsorption branches of the isotherms.

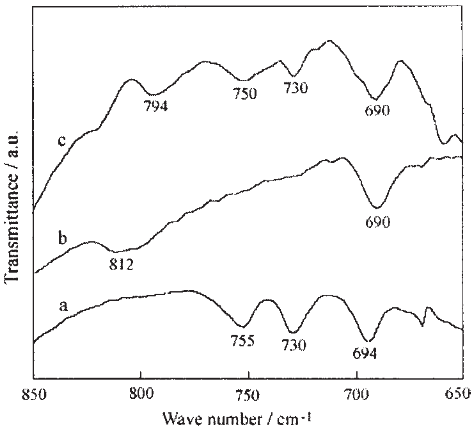

Figure 3. IR spectra of MZPPh (a), MZPPh-sul (b) and MZPPh-bro (c).

attaching the phenyl groups.[11] Furthermore, the chemical analyses provide the ratio P/Zr of 1.6 for the MZPPh sample, which is in accordance with the reported mesoporous zirconium phosphate.[6]

After the functionalization, although the ordering of the mesostructures of MZPPh-sul and MZPPh-bro decreased judging from the fact that the XRD peaks in their low angle region couldn't be identified, the existence of the mesopore morphologies is still clearly observed in the TEM images (Figures 2b and c). The texture properties of the sulphonated and brominated samples are further characterized by the N_2 adsorption experiments. Both functionalized samples show a slightly decreased surface area, ca. 300 m^2/g with a pore volume of 0.21 cm^3/g (MZPPh-sul) and 0.24 cm^3/g (MZPPh-bro). The brominated sample could roughly keep the original pore structure but the sulphonated sample presents a much dispersed mesopore distribution (Figure 1d), probably due to the corrosive effects of fuming sulphuric acid on the pore wall. The introduction of the $-SO_3H$ and $-Br$ on the phenyl groups in the samples is proved by their infrared spectra (Figures 3b and c). After sulphonating, the C–H vibration of phenyl group changed to 690 and 812 cm^{-1}, suggesting that almost all the phenyl groups have been sulphonated at the meta-positions.[10] However, for the brominated sample, besides the peak ascribed to the 1,3-double substituted phenyl ring (794 and 690 cm^{-1}), the C–H bands of original MZPPh still remain, which might be explained as the incomplete bromination reaction. The microcalorimetric measurements of NH_3 adsorption on MZPPh and MZPPh-sul were conducted to further confirm the introduction of the $-SO_3H$ groups in the latter sample (Figure 4). Compared with the unsulphonated sample, the strength of the acid sites on MZPPh-sul obviously enhanced as indicated by the increasing of the differential adsorption heat within the strong acid range. The results might also provide a pathway to prepare the solid acid catalyst through sulphonating the MZPPh. Further studies on the evaluation of the catalytic activities are presently in progress.

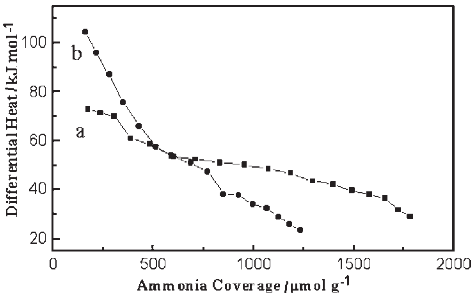

Figure 4. Microcalorimetric data of MZPPh (a) and MZPPh-sul (b).

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