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Generation of Brønsted acid sites on Si-MCM-41 by grafting of phosphorus species

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Phosphorus species could be grafted onto the surface of Si-MCM-41 by simply treating Si-MCM-41 with phosphoric acid for a very short period, followed by high temperature calcination. The existence and state of surface phosphorus species grafted on Si-MCM-41 are confirmed by XPS measurement. Using XRD and N_2 adsorption measurements, the uniform mesoporous structure of MCM-41 is shown to be quite stable under phosphoric acid treatment. FTIR results show that the surface phosphorus species grafted onto the surface of MCM-41 can selectively increase the number of Brønsted acid sites on the surface without forming any Lewis acid sites. Using NH_3–TPD, the mild acidity of the generated Brønsted acid sites on phosphorus-containing MCM-41 significantly enhances its catalytic activity for the dehydration of isopropanol.

1 Introduction

The discovery of highly ordered mesoporous materials (such as MCM-41, SBA-15, *etc.*) has attracted much attention due to their well-defined uniform mesopores (with tunable channel diameter from 2 to 30 nm) and their potential application as novel catalysts or catalyst supports for catalyzing large organic molecules and as novel adsorbents.[1–5] Metal-containing MCM-41 materials (prepared either by impregnation, ion-exchange or substitution) have been reported to have outstanding catalytic activities.[6–10] However, purely siliceous MCM-41 shows limited application for catalysis because of the lack of its acidity and capacity for ion-exchange. Although it is possible to improve the acidity and hydrothermal stability of Si-MCM-41 by incorporation of Al species into its framework,[11–17] however the incorporated aluminium has been proved not to be stable as the incorporated aluminium species may migrate from the framework to the surface.[18,19] Dealumination under thermal or hydrothermal treatment conditions can also form structural defects in the framework, blocking the pore channels of the mesoporous framework.[20] The incorporation of a small amount of aluminium in the framework of MCM-41 has also been shown to make its mesoporous structure less uniform.[18,21]

Furthermore, as compared with other zeolites, the amount of Brønsted acid sites on aluminosilicate MCM-41 material remains very low.[22] Due to the potential application of MCM-41 material as a catalyst for cracking big molecules, it is therefore important to prepare MCM-41 material possessing a uniform mesoporous structure and a high amount of Brønsted acid sites.

In this study, purely siliceous MCM-41 is post-synthetically acidified by external introduction of phosphorus species because the phosphorus species is shown not able to be directly incorporated into the framework of MCM-41 materials. In addition to the improvement of acidity, the phosphorus-containing catalyst is of interest because it has been reported to improve the activity of the catalyst for selective oxidation of hydrocarbon,[23–26] and to improve the hydrothermal stability of the resulting material.[26] The improvement of surface Brønsted acidity due to the grafting of phosphorus species on to MCM-41 is confirmed in this study by FTIR, NH_3–TPD and isopropanol dehydration reaction measurements.

2 Experimental

2.1 Material synthesis

Purely siliceous MCM-41 (designated here as Si-MCM-41) was prepared by hydrothermal synthesis using cetyltrimethylammonium bromide (CTMABr) as a template. The procedure was as follows: 6 g of aerosil and 2 g of NaOH was dissolved in 90 g of water under heating (60–70 °C) and stirring for approximately 30 min. This mixture was labeled as Mixture A. Mixture B was prepared by dissolving 9.1 g of CTMABr (99+%, Merck) in 50 g of water under heating (60–70 °C) and stirring for approximately 30 min. Mixture B was added dropwise to mixture A under stirring. The pH of the resulting mixture was adjusted to 11 using 2 M HCl solution. After additional stirring at room temperature for 3 h, the mixture was then transferred into a Teflon bottle and statically heated in the oven (100 °C) for 3 days. The resulting solid was recovered by filtration, washed with deionized water and dried at 50 °C. To remove the organic template, the as-synthesized MCM-41 was calcined at 600 °C for 10 h using a heating rate of 1 $°C\ min^{-1}$.

Another purely siliceous MCM-41 sample was synthesized in the presence of phosphoric acid in the gel mixture and then followed by a similar hydrothermal synthesis and calcination process as above. This sample is designated as Si-MCM-41(P).

Surface phosphorus species were externally introduced onto the surface of purely siliceous MCM-41 by impregnating 1 g of Si-MCM-41 sample in 4.5 ml of H_3PO_4 solution. In order to prevent the framework of Si-MCM-41 from being destroyed in the strong acid solution, the phosphoric acid impregnated MCM-41 sample was rapidly dried under stirring. It was then dried in the oven at 100 °C for 8 h and calcined at 400 °C for 3 h. By varying the concentration of phosphoric acid, three phosphorus-containing MCM-41 samples with Si/P = 100, 50, and 25 were prepared and designated here as PM-100, PM-50, and PM-25, respectively.

2.2 Material characterization

The surface phosphorus species was characterized by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS analytical instrument. A Mg K_α X-ray source ($h\nu$ = 1253.6 eV) with an analyzer pass energy of 80 eV was operated at 10 mA

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and 15 kV. The pressure in the XPS analysis chamber was less than 10^{-9} Torr. The binding energies of the XPS data were referenced to the C1s line at 284.6 eV with an accuracy of ± 0.1 eV and charge neutralisation was employed.

The pore size distribution of MCM-41 materials having phosphorus species on the surface was analyzed by nitrogen physisorption at 77 K using a Quantachrome Auto-Sorb1 Analyzer. Prior to nitrogen adsorption–desorption measurements, the sample was heated at 300 °C under vacuum for 2 h. The pore size distribution was calculated from the desorption branch of N_2 adsorption–desorption isotherms using the conventional Barrett–Joyner–Halenda (BJH) method, as suggested by Tanev and Vlaev.[27]

The powder X-ray diffraction patterns of phosphorus-containing MCM-41 samples were recorded using a Shimadzu XRD-6000 powder diffractometer, where Cu target Kα-ray (operating at 40 kV and 30 mA) was used as the X-ray source. The scanning 2θ range was from 1.5° to 10°.

The IR spectra characterizing the adsorption of pyridine on phosphorus-containing MCM-41 materials were recorded under vacuum using a Shimadzu FTIR-8700 spectrometer having a resolution of 2 cm^{-1}. 15 mg of sample was pressed at a pressure of 2 ton cm^{-2} for 30 min into a self-supported wafer (16 mm in diameter). Prior to the adsorption of pyridine, the sample was treated under vacuum ($<10^{-5}$ mbar) at 400 °C for 1 h. After the sample was cooled to room temperature, pyridine vapor was admitted to the IR cell for 30 min. After saturation, the sample was degassed at 100 °C.

The infrared spectra characterizing the surface hydroxy groups on unmodified and phosphoric acid-modified MCM-41 materials were recorded after treatment of the samples under vacuum ($<10^{-5}$ mbar) at 150 °C for 2 h.

Temperature programmed desorption (TPD) of NH_3 was performed in a quartz micro-reactor. 0.10 g of sample was firstly loaded in the reactor and heated in flowing He at 500 °C for 2 h. NH_3 was then introduced to the reactor after it was cooled down to room temperature. To remove the weakly adsorbed NH_3, the sample was swept using flowing He at 100 °C for 2 h. The TPD experiments were then carried out in flowing He with a flow rate of 40 ml min^{-1} from 100 to 500 °C at a linear heating rate of 10 °C min^{-1}. The desorption of NH_3 was detected by a Shimadzu GC-8A gas chromatograph equipped with a TCD detector.

The catalytic activity of the phosphorus containing MCM-41 catalysts for the dehydration of isopropanol was studied in a quartz microreactor containing 0.2 g of catalyst. Isopropanol was introduced to the reactor by flowing 20 ml min^{-1} of He saturated with isopropanol vapor at 20 °C. The concentration of the reaction products was analyzed by HP6890 GC equipped with a FID detector.

3 Results and discussion

Fig. 1 shows the XPS patterns of surface phosphorus species supported on MCM-41 materials. No binding energy peak of P_{2p} is observed on Si-MCM-41 because of the absence of phosphoric acid during its synthesis. Moreover, Si-MCM-41(P), which was synthesized in the presence of phosphoric acid in the gel mixture, does not even show any binding energy peak of P_{2p}, indicating that the phosphorus species can not be incorporated into the framework of MCM-41. Thus, the result shows that phosphorus-containing MCM-41 can not be directly synthesized by simply adding phosphorus acid into the synthesis gel.

P_{2p} XPS spectra for PM samples (Fig. 1) show that with an increase in phosphorus content, the XPS intensity of the P_{2p} peak on the phosphoric acid-modified samples increases. A small peak at the binding energy around 133.5 eV can be detected for the sample with Si/P = 100. This binding energy is not shifted with an increase in phosphorus content. A higher peak is detected at the same binding energy for the sample with Si/P = 25. The XPS results show that post-synthesis modification is an effective synthesis step to prepare phosphorous-containing MCM-41.

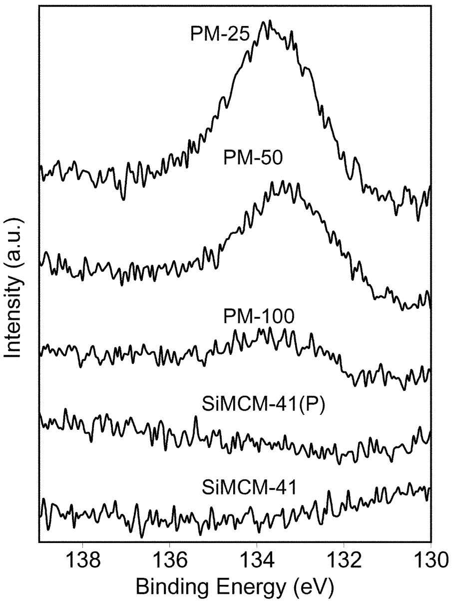


Fig. 1 XPS spectra characterizing P_{2p} on the surface of Si-MCM-41, PM-100, PM-50 PM-25, and Si-MCM-41(P).

Fig. 2 shows the XRD patterns of Si-MCM-41 and PM samples having different amounts of surface phosphorus species. A typical XRD pattern consisting of one large peak along with three small peaks, which is characteristic of MCM-41,[1,2] is observed for all samples. The result indicates that the uniformly-arranged hexagonal mesoporous framework is still well maintained even after the external loading of a large amount of phosphoric acid onto the surface of Si-MCM-41. Although the intensity of the [110] diffraction peak decreases along with the increase in phosphorus content, however the position of the (100) diffraction peak (at 2θ around 2.3°) remains almost the same for all PM samples. The d_{100} spacing of the PM sample, calculated based on the corresponding 2θ value, is almost not affected by post-synthesis modification with phosphoric acid. The preservation of the d_{100} spacing of the mesoporous framework upon treatment with phosphoric acid shows that phosphoric acid does not degrade the mesoporous framework but rather fills up the weakness in

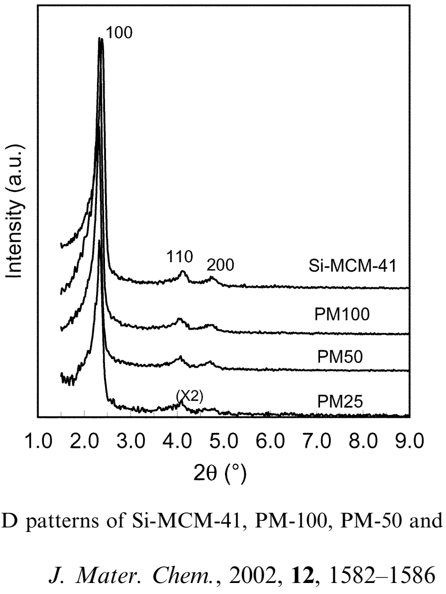


Fig. 2 XRD patterns of Si-MCM-41, PM-100, PM-50 and PM-25.

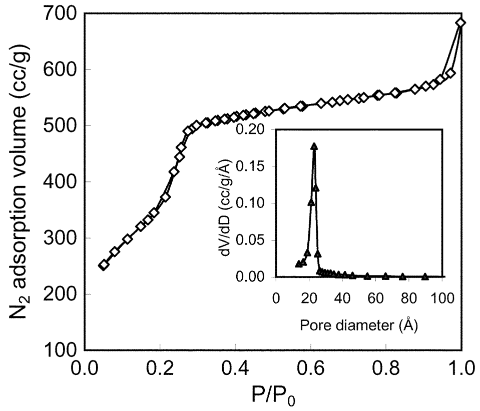


Fig. 3 N_2 adsorption–desorption isotherm and pore size distribution of PM-25.

the mesopore wall by the interaction of P–OH bonds in H_3PO_4 molecules with surface hydroxy groups.

Fig. 3 shows the result of N_2 adsorption–desorption isotherms and pore size distribution of PM-25, which has the highest phosphorus content in this study. The type IV isotherm obtained for this phosphorus-containing MCM-41 has the pore filling (by capillary condensation) restricted to a narrow range of $P/P_0 = 0.2$–0.3, which is a typical feature of MCM-41. As shown in Fig. 3, the pore size distribution of PM-25, which is calculated from the desorption branch of the N_2 adsorption–desorption isotherm, is very sharp. Both XRD and N_2 adsorption results show that the uniform framework and pore structure of MCM-41 could still be well maintained even after the external introduction of phosphorus species onto its pore surface during the impregnation of Si-MCM-41 material in phosphoric acid solution. Similar results have been observed by On *et al.*[28] during the treatment of MCM-41 in low or high pH solution; they reported that, although the framework of MCM-41 material could be destroyed very fast in high pH solution, however it was stable in an acid solution having a pH of 2 for 6 h.

Fig. 4 shows the *in situ* FTIR spectra of pyridine adsorption on the surface of Si-MCM-41 and PM samples after they have been degassed at 100 °C. Only hydrogen-bonded pyridine (having infrared bands at 1447 and 1600 cm^{-1}) is observed on Si-MCM-41. However, in addition to this hydrogen-bonded pyridine, an absorbance band at 1490 cm^{-1} is observed on the PM samples. This absorbance band is attributed to the adsorbed pyridine associated with both Lewis and Brønsted acid sites.[29] The intensity of this absorbance band increases with the amount of phosphorus on the surface of MCM-41, showing an increasing amount of acid sites on the pore surface of MCM-41 with an increasing amount of phosphorus species. In addition, Brønsted acid sites, which are characterized by two absorbance bands at 1545 and 1640 cm^{-1}, are clearly present on the PM samples. However, Lewis acid sites, which are characterized by two absorbance bands at 1450 and 1620 cm^{-1}, are not observed on the PM samples. The result indicates that most of the acid sites formed from phosphorus species on the surface of MCM-41 are Brønsted acid sites. It is interesting to note here that the effect of phosphorous species on the generation of acid sites on MCM-41 is different from the effect of aluminium species incorporated in the framework of MCM-41. Having Al incorporated in the framework of MCM-41, aluminosilicate MCM-41 has been reported to have both Lewis and Brønsted acid sites, with most of them having a substantial amount of Lewis acid sites.[11,30] In addition, both the amount of Lewis and Brønsted acid sites on Si-MCM-41 has also been found to be increased by post-synthesis alumination.[31] However, the results of this study show that post-synthesis modification of the surface of Si-MCM-41 by phosphoric acid can be used to selectively form a substantial amount of Brønsted acid sites on the mesoporous material without any formation of Lewis acid sites.

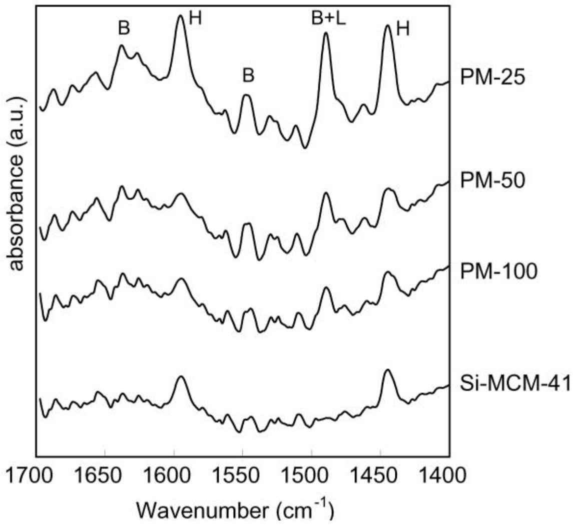
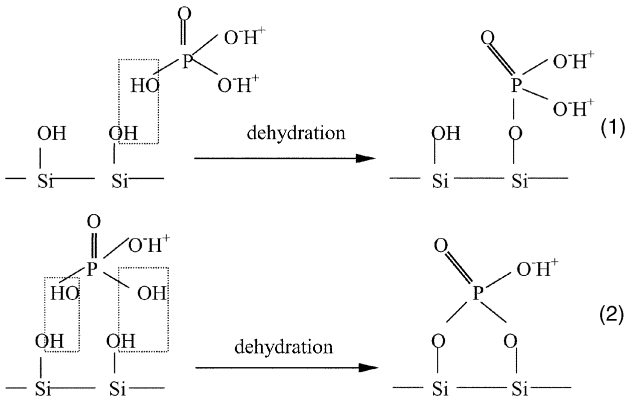


Fig. 4 FTIR spectra characterizing pyridine adsorption on Si-MCM-41, PM-100, PM-50 and PM-25.

The generation of Brønsted acidity on the phosphoric acid-containing MCM-41 material may be proposed to be due to the grafting of H_3PO_4 onto the surface of MCM-41. Scheme 1 shows two proposed reaction pathways for the generation of Brønsted acid sites from the grafted phosphorus species, which is formed from the dehydration of phosphoric acid attached on the hydroxy groups of Si-MCM-41. Reaction (1) shows that once H_3PO_4 is impregnated onto the surface of Si-MCM-41, there is an interaction between H_3PO_4 and one of the surface isolated OH groups. After calcination at high temperatures, a P–O–Si bond is then suggested to be formed by the dehydration of one water molecule, grafting the phosphorus species onto the surface of MCM-41. In another proposed reaction pathway, reaction (2) shows that H_3PO_4 may have interaction with two adjoining OH groups. After calcination at high temperatures, P–(O–Si)$_2$ bonds are then suggested to be formed by the dehydration of two water molecules, grafting the phosphorus species onto the surface of Si-MCM-41. Although the hydroxy groups of phosphorus acid can be removed by dehydration during high temperature calcination, the hydroxy groups of phosphorus can then also be restored after the adsorption of moisture in the air. These restored hydroxy groups on phosphorus still have the ability to donate H^+, producing mainly Brønsted acid sites on the surface of phosphorus-containing MCM-41.



Scheme 1 Two possible reaction pathways for the generation of Brønsted acid sites of the grafted phosphorus species, formed from the dehydration of phosphoric acid attached on the hydroxy groups of Si-MCM-41.

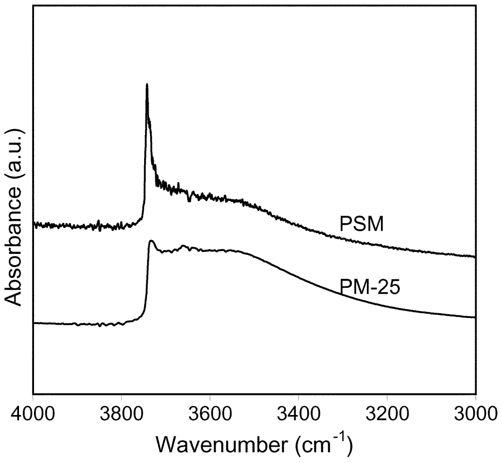


Fig. 5 FTIR spectra characterizing the surface hydroxy groups of Si-MCM-41 and PM-25.

Fig. 5 shows the IR spectra of Si-MCM-41 and PM-25. The sharp band at 3745 cm^{-1} is assigned to isolated Si–OH groups.[32] Having a considerable width at half height, the broad band at 3400–3730 cm^{-1} is assigned to hydrogen-bonded hydroxy groups.[33] After phosphorus species have been grafted onto the surface of Si-MCM-41, it can be observed that the intensity of the absorbance of isolated hydroxy groups becomes much weaker. The decrease of the concentration of isolated hydroxy groups on the surface of MCM-41 is attributed to the interaction of isolated OH groups with H_3PO_4. However, the intensity of the infrared absorbances between 3400 and 3730 cm^{-1} for PM-25 is stronger than that for Si-MCM-41. The result implies that the grafting of phosphorus species produces more hydrogen-bonded hydroxy groups, contributing to the increase in the amount of Brønsted acid sites on phosphorus-containing MCM-41. It is noteworthy that the improvement in the hydrothermal stability of the mesoporous framework—by minimizing the hydrolysis of Si–OH groups on the mesoporous framework by water molecules[26]—has also been attributed to the reduction in the amount of surface Si–OH groups due to their interaction with H_3PO_4 molecules.

The increase of the number and strength of the Brønsted acid sites over phosphorus-containing MCM-41 was further studied by the temperature programmed desorption of ammonia (NH_3–TPD). Fig. 6 shows the desorption profile of NH_3 from Si-MCM-41 and PM-25 samples. There is a very small amount of desorption of NH_3 from Si-MCM-41 as it lacks acid sites. However, the amount of NH_3 desorbed from the PM-25 sample is substantial, indicating that the number of Brønsted acid sites on phosphorus-containing MCM-41 can be substantially increased by simply grafting the phosphorus species onto its surface. This result is in good agreement with those obtained from the FTIR study of pyridine adsorption. Fig. 6 also shows that most NH_3 on the surface of PM-25 sample can be desorbed at temperatures between 150 and 300 °C. The NH_3–TPD result reveals that the acidity strength of Brønsted acid sites generated by the grafted phosphorus species on the surface of MCM-41 is relatively mild.[34]

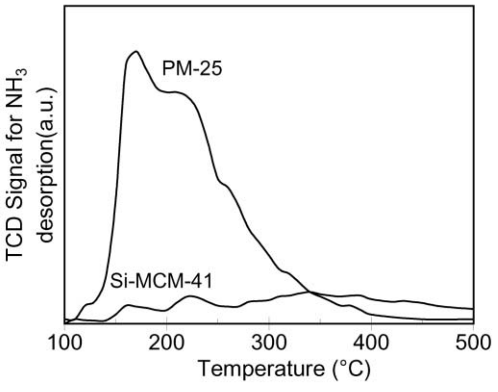


Fig. 6 NH_3–TPD profiles of Si-MCM-41 and PM-25.

Table 1 Conversion (%) of isopropanol to propylene over Si-MCM-41 and PM-25

	150 °C	175 °C	200 °C	250 °C	300 °C
Si-MCM-41	0	0	0.44	3.02	13.8
PM-25	5.60	10.1	47.1	97.3	99.9

Table 1 shows the steady state conversion values for the dehydration of isopropanol to propylene on Si-MCM-41 and PM materials. The steady state conditions were usually reached after about an hour on stream and the steady state conversions at a particular temperature were obtained at about 4 hours. As expected, due to the lack of acid sites, Si-MCM-41 has a very low activity for the dehydration of isopropanol; the conversion is $<1\%$ at 200 °C and only 3% at 250 °C. However, under the same reaction conditions, PM-25 has a conversion of 47.1% at 200 °C and 97.3% at 250 °C. The catalytic reaction results show that the Brønsted acid sites created by the external introduction of phosphorus species on MCM-41 can substantially increase the catalytic activity of the catalyst for the dehydration of isopropanol to propylene.

All the above results show that H_3PO_4-modified Si-MCM-41 is a promising selective catalyst for specific reactions that need only Brønsted acidity. Moreover, the idea of the simple post-synthesis modification of the mesoporous framework by phosphoric acid to generate Brønsted acid sites can also be extended to mesoporous materials other than MCM-41. In addition, the use of phosphoric acid can also be used to improve the hydrothermal stability of the mesoporous framework.

4 Conclusion

Simple external introduction of phosphorus species onto the surface of MCM-41 material could selectively and substantially increase the number of Brønsted acid sites without the formation of Lewis acid sites. The improvement of the Brønsted acidity of MCM-41 by simple post-synthesis introduction of surface phosphorus species is advantageous as the procedure does not cause any obvious deformation of the mesoporous structure of MCM-41. NH_3–TPD results reveal that the strength of the acidity created by phosphorus species on the pore surface of MCM-41 is relatively mild. Due to the improvement in its acidity, phosphorus-containing MCM-41 has a substantial catalytic activity for the dehydration of isopropanol to propylene.

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