Enhanced Acidity and Thermal Stability of Mesoporous Materials with Post-treatment with Phosphoric Acid

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The thermal stability and acidity of mesoporous materials can be greatly improved through the impregnation of phosphoric acid. The P-modified Al-MCM-41 shows potential application in the cracking of long-chain alkane for producing gas olefins, especially iso-butene.

The discovery of a new family of highly ordered mesoporous materials with uniform pore size in the range of 1.6-30 nm has greatly expanded the capacities of heterogeneous catalysis in comparison with zeolite materials.[1-3] It has been reported that the incorporation of Al species can result in potential acid catalysts. However, because of the amorphous character of mesoporous materials, the disadvantages of Al-MCM-41 — lack of strong acidity and lack of thermal or hydrothermal stability — would greatly limit their applications in acid catalysis.[4] Up to now, there are several routes related to the improvement on the thermal stability of mesoporous materials, such as pH adjustment,[5] ion-exchange,[6] salt effect[7] and surface silylanization.[8] Through these methods, the thermal stability of MCM-41 is largely improved due to the increase of aluminosilicate polymerization degree and the decrease of surface hydroxyl groups. The synthesis of mesoporous materials with increased wall thickness till 60 Å also greatly increase the thermal stability due to the reduction of weakness in the pore wall.[2] In general, because of the amorphous character of Al-MCM-41, the improvement of its acidity is a great challenge. Although efforts have been exerted on the crystallization of the mesopore wall, the results still show unsatisfactory.[9] In this paper, we put forth a simple and feasible method to increase both the acidity and thermal stability of mesoporous materials.

Different from the rigid framework of zeolite, the framework of mesoporous material is soft and can be shrunk after the removal of surfactant. By studying the kinetically destorying process of mesoporous materials during thermal or hydrothermal treatment, it is found that under high temperature, the d_{100} values gradually decrease before the total collapse of the mesostructure. It also represents for the gradual shrinkage of pore channel because of the over-condensation of surface hydroxyl groups. Thus, we can imagine that, the mesostructure would be greatly preserved by the impregnation of certain substance on its surface to resist the kinetic shrinkage of mesostructure. It is found H_3PO_4 is such an excellent candidate.[10,11] On the one hand, the P-OH bond in H_3PO_4 can react with the surface hydroxyl group to reduce the further condensation of the latter. Also, H_3PO_4 can fill up the weakness in the mesopore wall. On the other hand, H_3PO_4 can be polymerized to polyphosphoric acid with network structure at high temperatures. This network structure, which is tightly attached to the surface of mesostructure, can effectively resist the shrinkage of pore channel during thermal or hydrothermal treatment.

The P-modified mesoporous materials are prepared as follows. Firstly, Na-Al-MCM-41(Si/Al=14.2) was synthesized according to the procedure by Ryoo et al.[5] The product was calcined at 550 °C to remove surfactant cetyltrimetylammonium bromide (CTAB). Then, the calcined Na-Al-MCM-41 was impregnated with a calculated amount of H_3PO_4 solution at pH = 1-3 and temperature of 30 °C before dried at 100 °C. The samples were allowed for calcination at 550 °C for 4 h. The final products were denoted as P_1M41 and P_8M41, according to the H_3PO_4 impregnation amount of 1 wt% and 8wt % (P_2O_5 wt%), respectively. For comparison, H-Al-MCM-41 was prepared from ammonium exchanged Na-Al-MCM-41 at 70 °C for 2 h followed by calcination at 550 °C for 6 h. The thermal and hydrothermal stability test was conducted at 1000 °C for 0.5 h in dry Ar flow and at 800 °C steaming (100 % H_2O) for 2 h, respectively.

The XRD profiles of P_1M41 and P_8M41 have shown well-defined reflection peaks (100), (110), (200) and (210) compared with the calcined Na-Al-MCM-41, as well as a little decrease of d_{100} value and the intensity of (100) reflection peak (Figure 1). The BET areas also decrease from 939 m^2/g to 830 m^2/g after the impregnation of 8 wt% H_3PO_4 (Table 1). The results indicate that P-modified Na-Al-MCM-41 samples have only a few changes in the mesostructural integrity and pore parameters. However, H-Al-MCM-41 shows larger contraction of pore channel because of the dealumination during the ammonium-exchanging process and the following calcination. The thermal stability test indicates that even after calcination at 1000 °C, the XRD profile of P_8M41 still presents at least three diffraction peaks, representative of well-ordered hexagonal mesostructure (Figure 1), whereas H-Al-MCM-41 totally lost its mesostructure under the same condition. Likewise, under hydrothermal treatment at 800 °C, the percentage of pore channel shrinkage is only 13.0 % for P_8M41, compared with 19.5 % for Na-Al-MCM-41 and 22.3 % for H-Al-MCM-41. It indicates that the impregnation of H_3PO_4 can

Table 1. Post-synthetic impregnation of H_3PO_4 on Al-MCM-41 and the stability tests

Sample	Before Stability Test			Steaming treatment at 800 °C		Calcination at 1000 °C
	$S_{BET}/m^2/g$	pore size/nm	d_{100}/nm	d_{100}/nm	$S_{BET}/m^2/g$	d_{100}/nm
Na-Al-MCM-41	939	3.1	4.01	3.23	450	3.46
H-Al-MCM-41	870	3.1	3.76	2.92	--	destroyed
P_1M41	850	2.9	3.84	3.26	--	--
P_8M41	830	2.9	3.84	3.34	568	3.46

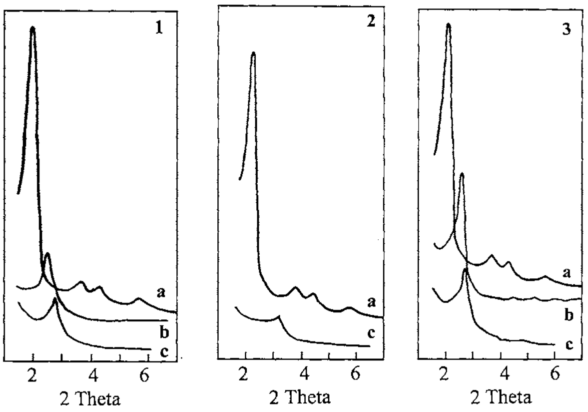

Figure 1. Effect of thermal and hydrothermal treatment of various Al-MCM-41 materials. (1) Na-Al-MCM-41, (2) H-Al-MCM-41 and (3) P_8M41. (a) before treatment, (b) calcined at 1000 °C for 0.5 h and (C) steaming treatment at 800 °C for 2 h.

effectively resist the mesopore shrinkage, thus resulting in less destroy of the mesostructure. Especially for P_8M41, it still has BET surface area of 568 m^2/g even after a strong steaming treatment at 800 °C.

It can be demonstrated that phosphoric acid can fill up the weakness in the mesopore wall by the interaction between P-OH and Si-OH. Moreover, it is suggested that the network polyphosphoric acid can be formed at high temperature, which also takes a very important role in maintaining the mesostructure by resisting the pore channel shrinkage. In addition, we can estimate, for 8 wt% H_3PO_4 impregnated on a mesoporous material with BET surface area of 830 m^2/g, the number of H_3PO_4 molecules distributed on MCM-41 surface ($\sim 8\times10^{20}/g$) is greatly lower than the number for a single layer loading ($\sim 8\times10^{21}/g$). Therefore, it indicates that the low loading of H_3PO_4, which has few changes to the intrinsic mesoporous property, shows good ability to improve the thermal stability of mesoporous material.

In addition to the improvement of thermal stability, the H_3PO_4 impregnation also afford mesoporous material with improved acidity. The NH_3-TPD results of P-modified Na-Al-MCM-41 show the acid strength has been greatly improved, as well as a little increase in the acid number. As shown above, the preparation of H-Al-MCM-41 from ammonium exchanged Na-Al-MCM-41 results in a great loss of thermal stability. Whereas H_3PO_4 can be directly impregnated on Na-Al-MCM-41 without further ammonium exchange, and the resulting P_8M41 possesses the similar acidity and reactivity for cracking n-alkane as H-Al-MCM-41 (Table 2). Although P_8M41 is less active for n-heptane cracking, it shows the similar activity to an industrial ZSM-5 catalyst for n-hexadecane cracking which requires only weak and medium acid sites. Compared with ZSM-5 catalyst, less gas products and more gasoline and kerosene (C_9-C_{14}) are produced for P_8M41 due to its relative medium acid strength. Moreover, the large surface area and small acid number (i.e. low acid density) could result in the decrease of hydrogen transfer reaction, so good selectivity can be achieved toward gas olefins for long-chain alkane cracking.[12] In addition, among the gas olefins $C_2^=$-$C_4^=$, the proportion of butene is as high as 54% compared with 40% for ZSM-5 catalyst. Thus, the reaction shows better selectivity toward iso-butene, which is an important source for producing MTBE — one of excellent gasoline additives. Therefore, the H_3PO_4 modified Na-Al-MCM-41, which has high thermal stability, medium acid strength and low acid density, can be better catalyst for the cracking of long-chain alkane for producing gas olefins, especially iso-butene.

Table 2. Comparison of cracking performance of n-alkanes over various samples (reaction temperature: 500 °C)

	Sample	ZSM-5 *	P_8M41	H-Al-MCM-41
Cracking reactivity/% Sample weight: 100 mg	n-C_7^o	10.3	3.3	3.2
	n-C_{10}^o	32.7	14.2	16.3
	n-C_{12}^o	67.0	24.8	32.5
	n-C_{16}^o	99.2	88.5	99.6
	Conversion of	n-C_{16}^o : ~	90%	
Selectivity/%	Gas (C_1-C_4)	75.8	62.8	66.7
	Liquid (C_5-C_{14})	24.2	37.2	33.3
	$C_2^=$ - $C_4^=$	62.9	53.5	56.7
	$iC_4^=$	16.8	18.6	18.1
Selectivity of gas products	Olefin/%	83	85	85
	$C_2^=:C_3^=:C_4^=$	10:50:40	3:44:54	3:47:50
	$C_4^o/C_4^=$	0.19	0.15	0.16
	$iC_4^=$ / $TC_4^=$	0.67	0.65	0.64

* aged with 100 % H_2O steam at 800 °C for 4 h.

In conclusion, by studying the kinetically destroying process of mesoporous materials, we find it is an effective route to improve the mesostructural stability by resisting the pore shrinkage during thermal treatment. The modification of H_3PO_4 has several specific advantages indicated above. Moreover, the idea of this method can also be expanded to the mesoporous materials other than MCM-41. The improvement of both thermal stability and acidity would make mesoporous material more competitive to act as acid catalysts.

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