

Synthesis, Characterization, and Catalytic Properties of SiPW-X Mesoporous Silica with Heteropolyacid Encapsulated into Their Framework

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A series of SiPW-X mesoporous silica with Keggin-type heteropolyacids (HPAs) encapsulated into their framework have been synthesized under strong acidic conditions. During hydrolysis of tetraethyl orthosilicate (TEOS), Na₂HPO₄ (P source) and Na₂WO₄ (W Source) are added into the initial sol-gel system to form Keggin type HPAs. The final products have been intensively characterized by various techniques, such as XRD, TEM, N₂ adsorption isotherm analysis, and by IR, UV/Visible, and ³¹P Magic Angle Spinning (MAS) NMR spectroscopy. Characterization results suggest that samples with an HPA weight percent of 13.3–20.7 % show very ordered hexagonal mesostructures. In addition, HPAs incorpo-

rated in the mesosilica are insoluble during catalysis. Results of catalytic tests show that SiPW-X materials have catalytic activities that are comparable to bulk HPA in catalytic tests implementing chemical reactions of both small (cumene cracking and esterification of ethanol with acetic acid) and bulky (1,3,5-triisopropylbenzene cracking and esterification of benzoic acid with *tert*-butanol) molecules. It can be readily separated from the reaction system for reuse, which suggests the potential industrial application.

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Introduction

The discovery of mesoporous materials (such as M41S, MSU and the SBA series) in the last decade has attracted much attention because of their potential uses as catalysts or catalyst supports in industrial applications.^[1–5] Incorporation of heteroatoms into mesoporous silica frameworks to form active sites in catalysis has been widely reported. For example, Al species have been introduced into the mesostructure and used as acidic catalysts in many catalytic reactions.^[6–13] In addition, mesoporous silica has often been used as a solid support in catalysis because of its high surface area and relatively large pore size. Some mesoporous materials with strong acidic sites on the surface have shown relatively high activities in many catalytic reactions.^[14–49]

It is well known that heteropolyacids (HPAs) with Keggin structures, especially 12-tungstophosphoric acid (HPW), have been widely applied in catalysis due to its strong acidity, facile preparation, and acceptable stability.^[32–49] However, the catalytic activities of HPAs are greatly limited because of their very low specific surface areas.^[16] Therefore, some researchers have carried on the

investigation of HPAs supported on mesoporous materials.^[14–31] For example, Corma et al. and Xia et al. have used HPAs supported on MCM-41 carriers, and these materials show high activity in isobutene alkylation and in the synthesis of MTBE.^[16,17] Nevertheless, their success and widespread use is limited for two reasons. First, HPA clusters block some pores causing the surface area of the modified mesoporous materials to be reduced significantly. Second, HPAs, from modified samples, leach into polar solvents leading to a decrease in catalytic activity and making it impossible to recycle in liquid-phase reactions.^[36] Some new synthetic routes and techniques for supporting HPAs on the porous materials have been reported that avoid these two problems.^[37–41] Hu et al. have prepared silica-supported Keggin-type HPAs by encapsulating HPAs into a silica matrix by a sol-gel technique involving the hydrolysis of tetraethoxysilane (TEOS).^[40] Recently, Nowińska et al. have reported the incorporation of HPAs into mesoporous materials by introducing the HPA into the sol-gel during the hydrolysis of TEOS in the preparation of SBA-3.^[41] However, after heating to reflux in methanol, HPA is extracted and the mesostructure collapsed. The relatively low stability of the materials can be attributed to their relatively thin wall thickness.

It has been widely reported that mesoporous silica of SBA-15 has been extensively used as support and host because of its larger pore size, thicker wall and higher hydrothermal stability than MCM-41 (SBA-3).^[4,5] We have introduced Na₂HPO₄ (P source) and Na₂WO₄ (W Source) into the initial sol-gel during preparation of SBA-15 and suc-

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cessfully synthesized new mesoporous silica encapsulated with Keggin-type HPA. Here, we report the synthesis, characterization, and catalytic properties of SiPW-X mesosilica with Keggin-type 12-tungstophosphoric acid (HPW) encapsulated into their framework.

Results and Discussions

Spectroscopy

X-ray Diffraction

Figure 1 shows small-angle powder XRD patterns of SiPW-X samples with various HPW content. Obviously, the mesostructure ordering of the samples gradually decreases with increasing HPW content. The samples of SiPW-16 and SiPW-8 (Figure 1b and c, and Table 1) exhibit three well-resolved peaks indexed as (100), (110), and (200), which can be associated with $p6mm$ hexagonal symmetry that is similar to that of pure silica SBA-15 (Figure 1a).^[4,5] In fact, the ordering of the samples with high HPW content is very small. For example, sample SiPW-4 only gives one broad peak (Figure 1d) and sample SiPW-2 gives no obvious diffraction pattern (Figure 1e). These results indicate that the content of HPW in mesosilica with a highly ordered struc-

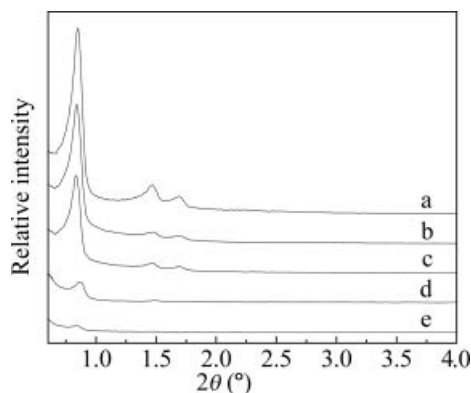


Figure 1. Small-angle XRD patterns of various samples: (a) SBA-15, (b) SiPW-16, (c) SiPW-8, (d) SiPW-4, and (e) SiPW-2.

Table 1. HPW content and parameters for the pore structure of SiPW-X, SBA-15, HPW, and HPW/SBA.

Samples	HPW content		<i>d</i> (nm)	<i>a</i> (nm)	Pore size (nm)	Wall thick- ness (nm) ^[a]	BET surface area (m ² /g)	Pore volume (cm ³ /g)
	sol-gel (wt.%)	Product (wt.%)						
SiPW-4	50.0	23.2	10.2	11.8	6.8	5.0	570	0.77
SiPW-8	33.2	20.7	10.6	12.2	7.5	4.7	805	0.94
SiPW-16	20.0	13.3	10.5	12.1	7.6	4.5	828	1.03
SBA-15	0.0	0.0	10.3	11.9	7.9	4.0	860	1.15
HPW/SBA	20.0	20.0	10.2	11.8	7.8	4.0	366	0.65
HPW	100	100	-	-	-	-	7	-

[a] Pore size distributions were determined from N₂ adsorption isotherms, and the wall thickness was calculated as: thickness = $a - \text{pore size}$ ($a = 2d_{(100)}/3^{1/2}$).

ture is 13.3–20.7 wt.-%. Additionally, the only difference in the XRD patterns of pure silica SBA-15, SiPW-8, and SiPW-16 is the intensity of the three observed diffraction peaks (Figure 1), and this suggests that the formation of HPW by the addition of Na₂HPO₄ and Na₂WO₄ into the sol-gel during the hydrolysis of TEOS does not disturb the formation of the mesoporous structure. Moreover, wide-angle powder XRD patterns recorded for modified samples (not given) do not show any obvious characteristic signals for HPW, indicating very high HPW dispersion in the mesosilica matrix.^[30]

Transmission Electron Microscopy

TEM images of mesoporous samples with varied HPW content are shown in Figure 2. Obviously, the pores of all the samples are hexagonal analogous to those of pure silica SBA-15.^[4,5] Compared with Figure 2c–f, the images shown in Figure 2a and b suggest that the ordering of the SiPW-4 sample is less than that of the SiPW-8 and SiPW-16 samples, which is in agreement with the results of XRD. Moreover, it can also be observed that there are many out-of-order components deposited in the mesoporous channels of

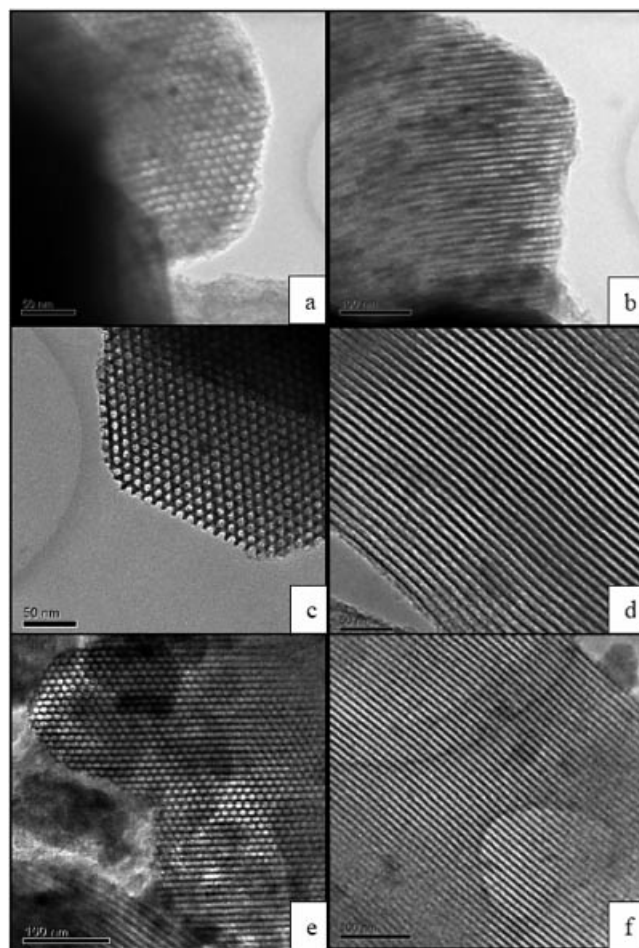


Figure 2. TEM images of various samples: (a) SiPW-4 in [100] direction, (b) SiPW-4 in [110] direction, (c) SiPW-8 in [100] direction, (d) SiPW-8 in [110] direction, (e) SiPW-16 in [100] direction, and (f) SiPW-16 in [110] direction.

the SiPW-4 sample (Figure 2a and b). The weight content of HPW in the SiPW-4 sample is a little higher (23.2%) than those of the other samples. Therefore, some HPW species cannot be incorporated into the wall of the mesoporous silica but rather be deposited in the mesoporous channels as small, silica-HPW domains.

N₂ Adsorption Isotherms

Figure 3 shows the N₂ adsorption isotherms of the SiPW-X samples with varied HPW content. The porous parameters are listed in Table 1. Obviously, SiPW-8 and SiPW-16 show a typical adsorption curve of type IV with an obvious hysteresis loop at a relative pressure of $0.6 < P/P_0 < 0.9$ (Figure 3c and d), which is very similar to that of pure silica SBA-15.^[4,5] However, increasing the content of HPW leads to a decrease in surface area and pore volume. For example, the Brunauer, Emmett and Teller (BET) surface area and pore volume of SiPW-16 were found to be 828 m²/g and 1.03 cm³/g, the corresponding values of SiPW-8 and SiPW-4 were 805 m²/g and 0.94 cm³/g, and 570 m²/g and 0.77 cm³/g, respectively. Additionally, there is no obvious difference in the porous parameters of pure silica SBA-15 and of the SiPW-8 and SiPW-16 samples, indicating the formation and presence of HPW in the initial gel does not disturb the formation of the mesostructure, which is in agreement with the XRD results.

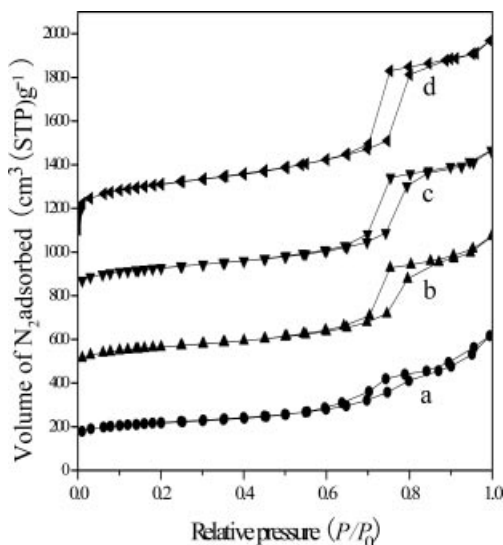


Figure 3. N₂ adsorption/desorption isotherms of various samples at STP: (a) SiPW-4, (b) SiPW-8, (c) SiPW-16, and (d) SBA-15.

IR Spectra

Infrared spectra of various samples are shown in Figure 4. It has been widely reported that HPWs with Keggin structures give several strong, typical IR bands at ca. 1080 cm⁻¹ (stretching frequency of P–O in the central PO₄ tetrahedron), 983 cm⁻¹ (terminal bands for W=O in the exterior WO₆ octahedron), 889 and 803 cm⁻¹ (bands for the W–O_b–W and W–O_c–W bridge, respectively)^[21,22,24] [Figure 4a]. It is well known that pure mesoporous SBA-15 silica shows framework bands at 805 cm⁻¹ (symmetric stretch-

ing frequency of Si–O–Si), 960 cm⁻¹ (stretching frequency of Si–O–H), 1060–1100 cm⁻¹ (*anti*-symmetric stretching of Si–O–Si) [Figure 4d]. In our case, the SiPW-8 and SiPW-16 samples give bands at 1080, 963, 890, 803 cm⁻¹ and one shoulder band at 982 cm⁻¹ in the 600–1400 cm⁻¹ region (Figure 4b and c). The band at 890 cm⁻¹ and the weak shoulder band at 982 cm⁻¹ can be attributed to the characteristic Keggin type HPW W–O_b–W bridge and the terminal W=O, respectively,^[21] the broadened bands at 1080 and 800 cm⁻¹ are the characteristic bands of HPW, which overlap with the bands of mesoporous SBA-15.^[22,43] These results confirm the presence of HPW encapsulated into the mesoporous silica framework.

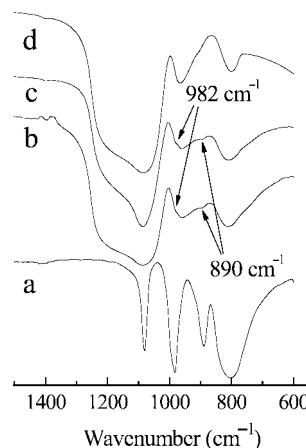


Figure 4. IR spectra of various samples: (a) HPW, (b) SiPW-8, (c) SiPW-16, and (d) SBA-15.

UV/Visible Diffuse Reflectance Spectra

Some evidence of the presence of HPW in the mesoporous silica framework is also provided by UV/Visible spectroscopy. The UV/Visible spectra of mesoporous samples with varied HPW content are shown in Figure 5. Bulk HPW shows a maximum UV absorption peak at 265 nm, which is attributed to the oxygen–tungsten charge-transfer absorption band for Keggin anions^[40] (Figure 5a). Pure SBA-15 silica shows no UV absorption (Figure 5d). In our case, both SiPW-8 (Figure 5b) and SiPW-16 (Figure 5c) samples have a broad UV absorption in the range of 200–300 nm – a characteristic UV absorption peak is centered at 263–266 nm, which is similar to that of the PW₁₂O₄₀³⁻ species. These results indicate that the primary Keggin structure has been introduced into the mesostructure framework and is very stable even after the surfactants are extracted and washed by deionized water; this is in agreement with the IR results.

³¹P MAS NMR Spectra

Figure 6 shows the ³¹P MAS NMR spectra of SiPW-8 and HPW. The spectrum for bulk HPW, consisting of a single peak at –15.3 ppm, agrees well with the literature data.^[16,46] The spectrum for SiPW-8 is practically the same as that of bulk HPW with one signal at –15.3 ppm, which is attributed to homogeneously dispersed HPW clusters that

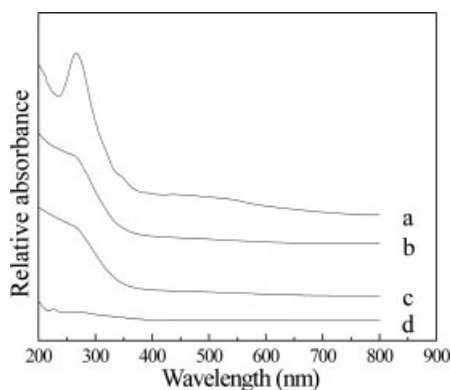


Figure 5. UV/Visible spectra of various samples: (a) HPW, (b) SiPW-8, (c) SiPW-16, and (d) SBA-15.

retain the Keggin structure; however, there is another resonance of lower intensity at -14.1 ppm. This new signal at -14.1 ppm may be induced by chemical interactions of HPW with the framework of the mesoporous material, which is constituted of a network of SiO_2 .^[46]

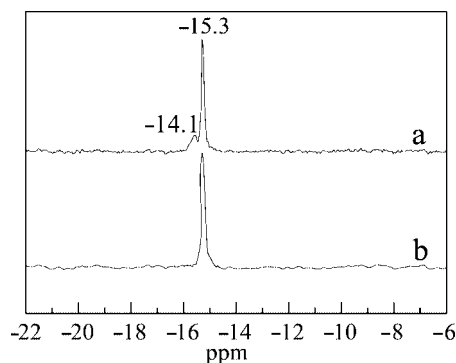


Figure 6. ^{31}P MAS NMR spectra of: (a) SiPW-8 and (b) HPW.

Catalytic Results

Cumene Cracking

The cumene cracking reaction is used to evaluate the acidity of the samples. As shown in Table 2, mesoporous

pure silica (SBA-15) shows a very low catalytic activity (conversion at 1.2%) in this reaction. All SiPW-X samples show relatively high catalytic activities. The conversion of cumene is 13.7% for the reaction with the SiPW-16 sample, while a higher catalytic activity, with a conversion of 28.6%, is observed for the reaction with SiPW-8. It has been reported that HPW supported on the surface of SBA-15 by the impregnation method give cumene cracking conversions of 46.1 and 5.7%, with the weight content of HPW at 40 and 20%, respectively.^[43] In our case, HPW supported on the surface of SBA-15 prepared by the same method gives 9.1% conversion with a weight content of HPW at 20%, and SiPW-8 shows much higher conversion (28.6%) with a similar HPW weight content. These results indicate that HPWs have been well encapsulated in the mesoporous framework and show good catalytic activities.

TIPB Cracking

In TIPB cracking, as shown in Table 2, pure SBA-15 silica shows low catalytic activity (3.8%) and, according to previous reports, HPW supported on the surface of MCM-41 by impregnation methods gives a conversion of 55%, with an HPW weight content of 23%.^[30] In our case, SiPW-8 (20.7 wt.-%) and SiPW-16 (13.3 wt.-%) show high catalytic activities and give conversions of 70.2 and 58.5%, respectively, which are higher than those of previous reports.^[30] The results suggest the potential use of these compounds as catalysts for bulky molecule catalysis.

Esterification of Acetic Acid with Ethanol and of Benzoic Acid with *tert*-Butanol

In the esterification of acetic acid with ethanol, the SiPW-16 and SiPW-8 samples give conversions of 17.2 and 31.5%, respectively. HPW/SBA prepared by the impregnation method shows a similar catalytic activity (32.3%). Moreover, after the catalysts were reused five times (Table 2), the SiPW-8 and SiPW-16 samples still showed catalytic activities similar to those of the fresh catalysts, while that of HPW/SBA prepared by the impregnation method decreases remarkably, which is attributed to the leaching of HPW supported on the surface of SBA-15.^[36]

Table 2. Catalytic activity of SiPW-X, SBA-15, HPW, and HPW/SBA, and the element analysis of spent catalysts and liquid solution for P- and W content.

Samples	Conversion of cumene (wt. %)	Conversion of TIPB (wt. %)	Conversion 1 ^[a] (wt. %)		Conversion 2 ^[b] (wt. %)		P content		W content	
			fresh	used ^[c]	fresh	used ^[c]	sc ^[d]	ls ^[e]	sc ^[d]	ls ^[e]
SiPW-8	28.6	70.2	31.5	30.9	10.3	10.1	0.223	≈ 0	15.9	≈ 0
SiPW-16	13.7	58.5	17.2	17.0	7.5	7.2	0.143	≈ 0	10.2	≈ 0
HPW/SBA	9.1	19.7	32.3	3.4	3.8	0.7	0.009	0.04	0.64	0.51
HPW	35.8	53.5	50.8	—	8.0	—	—	—	—	—
SBA-15	1.2	3.8	1.5	1.0	0	0	—	—	—	—

[a] Esterification reactions of acetic acid with ethanol. [b] Esterification reactions of benzoic acid with *tert*-butanol. [c] The catalysts were used five times. [d] Spent catalysts (sc) in esterification reactions of benzoic acid with *tert*-butanol after being used five times, the units for P- and W content are wt.-%. [e] Liquid solution (ls) in esterification reactions of benzoic acid with *tert*-butanol after separation of the catalysts after being used five times, the units for P- and W content are $\times 10^{-3}$ mmol/ml.

Similar phenomena have also been observed in the esterification of benzoic acid with *tert*-butanol. The SiPW-16 and SiPW-8 samples give conversions of 7.2 and 10.1%, respectively, even after being reused five times, while the HPW/SBA samples only show a conversion of 0.7% after five uses. The above results suggest that the SiPW-X samples are very stable in liquid reactions even when reused many times, and leaching of HPW in these samples is hardly observed relative to that in the samples prepared by the impregnation method.

In order to help the reader better understand the difference between SiPW-X and HPW/SBA prepared by the impregnation method, we give a simple schematic model of SiPW-X (bottom part of Figure 7). We also give a schematic model of the interactions of silicon species with heteropolyanions under strong acidic conditions during preparation of SiPW-X (top part of Figure 7) and of terminal silicon hydroxyl groups of SBA-15 with heteropolyanions during preparation of conventional SBA-15 supported HPW (Figure 8). From Figure 7 and 8, we can see that the interaction of the silicon species with the heteropolyanions under strong acidic conditions is much stronger than that of the terminal silicon hydroxyl groups of SBA-15 with the heteropolyanions. Therefore, the stability of the composite materials (SiPW-X) comes from the fact that HPW is dispersed in the silica wall.

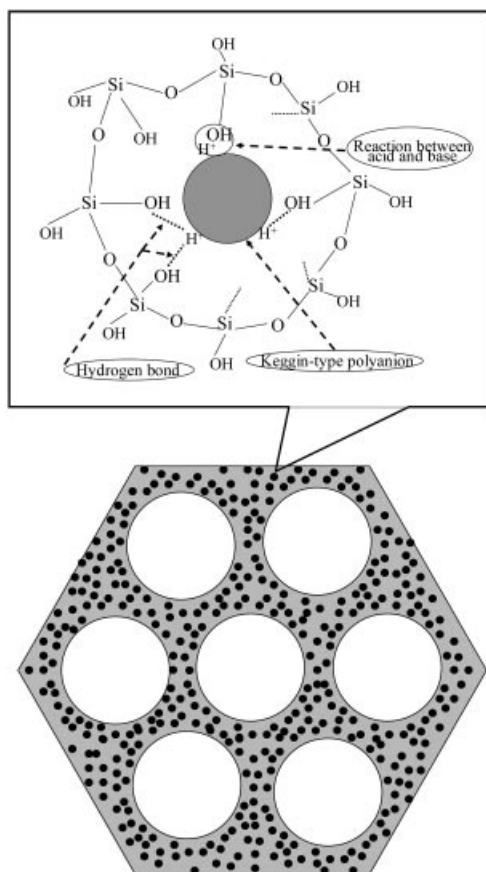


Figure 7. Simple schematic model of the interaction of the silicon species with heteropolyanions under strong acidic conditions during preparation of SiPW-X.

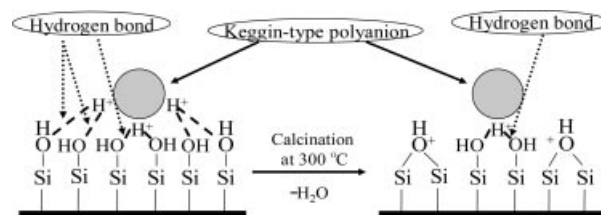


Figure 8. Simple schematic model of the interaction of terminal silicon hydroxyl groups of SBA-15 with heteropolyanions during preparation of conventional SBA-15 supported HPW.

In summary, the SiPW-X mesosilica materials with Keggin-type heteropolyacids encapsulated into their framework are excellent acidic catalysts for both small and bulky molecules. Additionally, other properties, such as easy separation, reusability etc., ensure the potential use in industrial applications.

Conclusion

Mesoporous silica with Keggin-type heteropolyacids encapsulated into their framework has been synthesized by addition of Na_2HPO_4 and Na_2WO_4 into the initial sol-gel system during hydrolysis of TEOS under strong acidic conditions. Characterization results suggest that samples with HPA contents of 13.3–20.7 wt.-% show very ordered hexagonal mesostructures. The HPA incorporated in the mesosilica is insoluble during catalysis. Catalytic cracking results suggest that these samples are very active in both small molecule (cumene) and bulky molecule (1,3,5-triisopropylbenzene) reactions. Additionally, esterification results in liquid reactions (polar solvent) after recycling indicate that these materials can be easily separated and recycled.

Experimental Section

Materials: Tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl), cumene, benzoic acid, tertiary butanol, ethanol, and acetic acid were of analytical grade and purchased from Tianjin Chemical Co. (China). Sodium tungstate (Na_2WO_4) and sodium monohydrogen phosphate (Na_2HPO_4) were of analytical grade and supplied by Beijing Chemical Co. (China). $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123) and 1,3,5-triisopropylbenzene (TIPB) were from Aldrich.

Synthesis: The typical synthesis process was as follows: (1) Pluronic P123 (4.0 g) was dissolved in a solution of deionized water (100 mL) containing hydrochloric acid (20 mL, 36 wt.-%), followed by addition of TEOS (10 mL). The mixture was stirred at 40 °C for 3 h. (2) A requisite amount of Na_2WO_4 and Na_2HPO_4 was added simultaneously to the above mixture to form a white precipitate. (3) The mixture was further stirred at 40 °C for 20 h and then transferred to a stainless steel autoclave for crystallization at 100 °C for 48 h.

The obtained products were collected and dried in vacuo ($<10^{-2}$ Pa) at 150 °C for 6 h and washed with an ethanol solution containing HCl and distilled water three times, and finally dried in vacuo ($<10^{-2}$ Pa) at 300 °C for 5 h. The final products were desig-

nated as SiPW-X, where X stands for the Si/W molar ratio in the initial gel.

For comparison, pure silica SBA-15 and HPW were synthesized according to the literature procedures;^[15,42] conventional SBA-15 supported HPW was made by immersing SBA-15 powder into an HPW solution for 3 h followed by drying at 100 °C for 24 h, and then calcining at 300 °C for 5 h; this is denoted as HPW/SBA.

Characterization: Powder X-ray diffraction (XRD) data were recorded on a Siemens D5005 (30 kV, 30 mA) using nickel-filtered $\text{Cu-K}\alpha$ radiation with a wavelength of $\lambda = 0.15418$ nm, diffraction patterns were collected under ambient conditions in the 2θ range of $0.6\text{--}4^\circ$ at a scanning rate of $0.6^\circ/\text{min}$ and in the 2θ range of $4\text{--}70^\circ$ at a scanning rate of $6^\circ/\text{min}$. Transmission electron microscopy (TEM) experiments were performed on a JEM-3010F electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The nitrogen isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. Infrared (IR) spectroscopy was performed on a Bruker IFS 66v/S infrared spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets in vacuo (<0.4 Pa) at ambient temperature. The diffuse reflectance UV/Visible spectra for powder samples were obtained on a Perkin-Elmer Lambda 20 UV/Visible spectrometer equipped with an integrating sphere, with BaSO_4 as an internal standard. Solid-state ^{31}P NMR experiments were performed with magic angle spinning (MAS) on an Infinity Plus-400 spectrometer operating at a frequency of 104.26 MHz, chemical shifts were referenced to 85% H_3PO_4 as an external standard. The HPW content in solid samples were determined by the results of inductively-coupled plasma analysis (ICP, Perkin-Elmer 3300DV).

Catalytic Test

Catalytic Cracking of Cumene and 1,3,5-Triisopropylbenzene (TIPB): Catalytic cracking of cumene and 1,3,5-triisopropylbenzene were carried out using the pulse technique in a micro-reactor, and the analyses of the catalytic products were performed by gas chromatography (GC-17A, Shimadzu Co.) equipped with a flame ionization detector (FID). The catalytic cracking was performed according to the following standard conditions: the reaction temperature was 300 °C (no thermal cracking); the reaction pressure was atmospheric pressure; the mass of the catalyst was 0.050 g; 0.2 μL of cumene or 1,3,5-triisopropylbenzene was injected for each test; nitrogen was used as the carrier gas at a flow rate of 45 mL/min.

Esterification of Acetic Acid with Ethanol and of Benzoic Acid with *tert*-Butanol: The esterification of acetic acid with ethanol was performed under nitrogen at 40 °C in a flask (50 mL) containing suspended catalyst powder (60 mesh pass), acetic acid (0.15 mol), and ethanol (0.15 mol), and with vigorous agitation for 4 h. The amount of catalyst used was 0.10 g. The product esters were analyzed by gas chromatography (6890N, Agilent Co.) equipped with a flame ionization detector (FID) with an HP-5 flexible quartz capillary column (30 m in length).

The esterification of benzoic acid with *tert*-butanol was performed under nitrogen at 80 °C in a flask (50 mL) containing suspended catalyst powder (60 mesh pass), benzoic acid (5 mmol), and *tert*-butanol (10 mmol), and with vigorous agitation for 5 h. The amount of catalyst used was 0.10 g. The product esters were analyzed by gas chromatography (6890N, Agilent Co.) equipped with a flame ionization detector (FID) with an HP-5 flexible quartz capillary column (30 m in length).

Acknowledgments

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