

Preparation, characterization and catalytic activity of heteropolyacids supported on mesoporous silica and carbon

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HPA was impregnated on mesoporous silica (SBA-15, MCM-41), commercial silica (ML369) and activated carbon, as well as on mesoporous carbons (CMK-1, CMK-3). The resulting materials were investigated by means of XRD, BET and catalytic probe reactions of liquid-phase esterification of hexanoic acid with propanol-1 and acylation of 2-methoxynaphthalene with acetic anhydride. The catalytic performance was optimal with loading of around 40wt% HPA. $H_3PW_{12}O_{40}$ (PW) was more active than $H_4SiW_{12}O_{40}$ (SiW) for esterification, irrespective of the supports used. Solvent used in the impregnation and hydrophobic/hydrophilic nature of the support could influence the performance of the catalyst in these acid catalyzed reactions.

1. INTRODUCTION

Heteropolyacids (HPAs) have stimulated considerable research in both heterogeneous and homogeneous catalysis [1-3]. Among them, 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (PW), the strongest and the most stable acid in the Keggin series of HPAs, has attracted the most attention. The main drawback of such materials for catalytic application is their low specific surface area. Thus, direct dispersion of the bulk HPAs on a mesoporous silicate support such as MCM-41 [4], commercial silica, and activated carbon [5] has been attempted. SBA-15 [6] possessing larger pore size and CMK-1,3 [7] are mesoporous materials newly emerged recently, and have not been tested as a carrier for supporting HPAs. Here we report the comparison of mesoporous silica (SBA-15, MCM-41), commercial silica (ML369), activated carbon and mesoporous carbon (CMK-1, CMK-3) supported HPAs as catalysts for the liquid phase esterification and acylation reactions.

2. EXPERIMENTAL

MCM-41 was synthesized according to the literature recipe [4]. SBA-15 was synthesized by using the triblock copolymer, $EO_{20}-PO_{70}-EO_{20}$ (Pluronic 123, BASF) as the surfactant and the tetraethylorthosilicate (TEOS, 98% Aldrich) as silicon source [6]. The supported HPAs catalysts were prepared by impregnation of HPAs on various carriers following the procedure

of Kozhevnikov et al [2]. Typically, the required amount of HPAs was dissolved in various solvent and a proportional amount of the support material were added. The mixture was stirred for 18h at room temperature. Subsequently, solvent was removed in a rotary evaporator, yielding the HPA-impregnated catalysts. The material was dried and mildly calcined at 403K and stored in a desiccator until use. XRD patterns were obtained with a $\text{CuK}\alpha$ X-ray source (Rigaku Miniflex instrument, 450W). N_2 -adsorption isotherms were obtained at 77K using a Micromeritics ASAP2000. The samples were outgassed at 403K and 0.1Pa for 12h before measurements were performed. Specific surface areas were obtained with the BET equation; the mean pore sizes by the BJH method. Esterification of hexanoic acid with propanol-1 was carried out at reflux temperature in a glass vessel equipped with a magnetic stirrer and a Dean Stark trap for water removal. Toluene was used as a solvent. Acylation of 2-methoxynaphthalene with acetic anhydride was carried out at 323 K using chlorobenzene as a solvent. Analysis was performed with GC (ShimadzuGC-14A) equipped with Shimadzu column Hicap CBP1-M25-025 with a flame ionization detector.

3. RESULTS AND DISCUSSION

As shown in Fig.1, the introduction of 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW) to mesoporous silica SBA-15 or mesoporous carbon CMK-3 resulted in little decreases in intensities of the XRD reflections of the mesostructures, which suggests that the structural order of the host materials is maintained. In addition, no peaks corresponding to HPA were detected indicating highly dispersed state of HPA impregnated. The preparation conditions such as the heteropoly anionic species, physicochemical properties of the supports, the impregnation solvent, and the loadings of HPAs were shown to have pronounced influences on catalytic performances (shown in Figs. 2-5). $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW) was more active HPA than $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW) for esterification, irrespective of the supports used. Catalytic performance was optimal with loading of around 40wt% HPA. Apparently, the higher the HPA loadings, the higher would be the catalytic activity due to generation of increased active sites, but loadings of 50% or more must have caused blockage in the support channels and also resulted

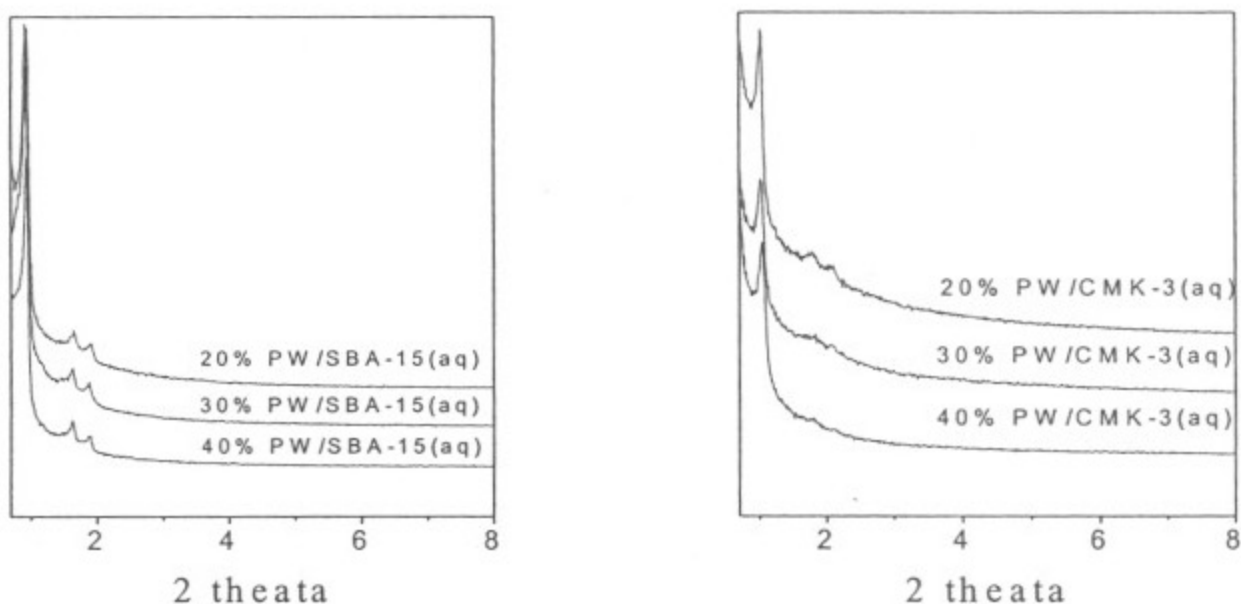


Fig. 1. XRD Patterns after different loadings of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on SBA-15 and CMK-3

Table 1

Surface areas and porosities of SBA-15 impregnated with PW

Samples	BET surface area (m ² /g)	BJH average diameter (Å)	Pore volume (cc/g)
30%PW/SBA-15 (aq)	425	64.1	0.60
40%PW/SBA-15 (aq)	292	61.0	0.44
50%PW/SBA-15 (aq)	207	59.8	0.31

in poor dispersion. As shown in Table 1, when the amount of PW introduced to SBA-15 was 30wt%, 40wt%, 50wt%, the surface area and pore volume varied correspondingly as 425, 292, 207 m²/g and 0.60, 0.44, 0.31 ml/g, respectively. These changes can be explained by the large molecular size of the Keggin anion (1.2 nm in diameter) and its interaction with the amorphous wall of the host material. In the hexanoic acid esterification, following catalytic activity order of PW supported on different silica impregnated in aqueous phase was obtained: PW/SBA-15 > PW/MCM-41 > PW/silica. This difference can be explained in terms of the larger pore size of SBA-15 than MCM-41 and bigger surface areas of the mesoporous materials than

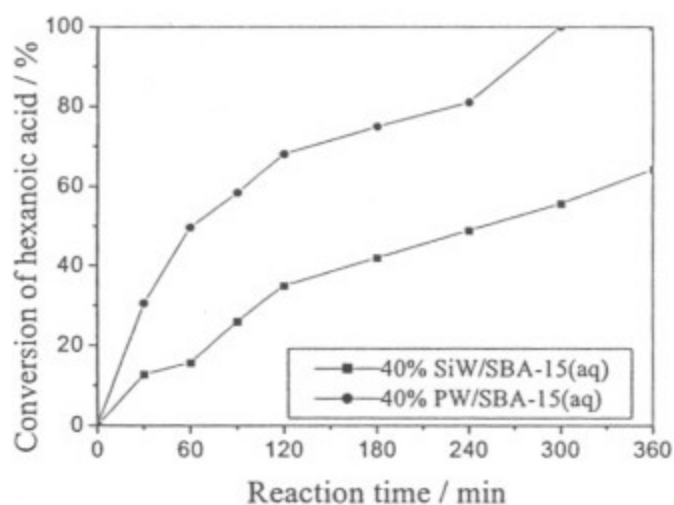


Fig. 2. Catalytic performance of different HPAs on SBA-15.

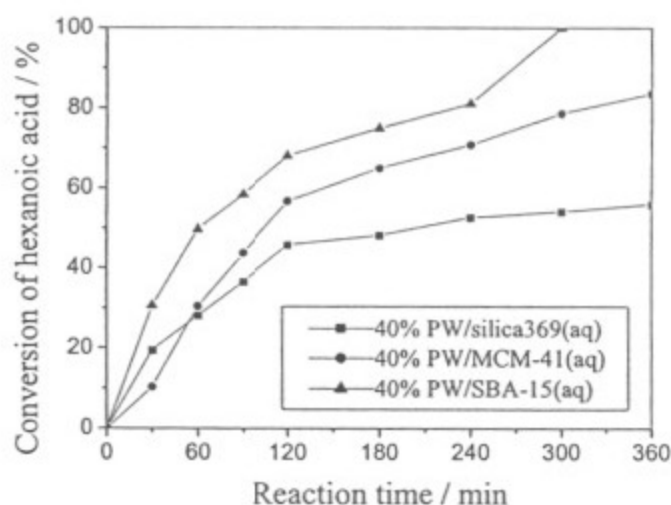


Fig. 3. Effect of different silica supports on catalytic performance.

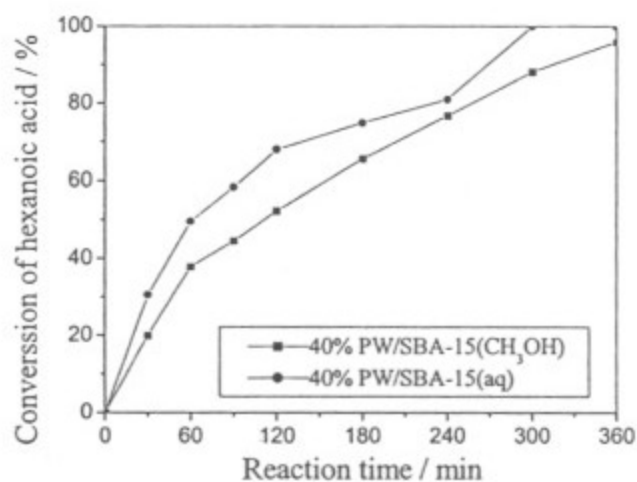


Fig. 4. Effect of impregnating solvent for HPA on catalytic performance (SBA-15 support)

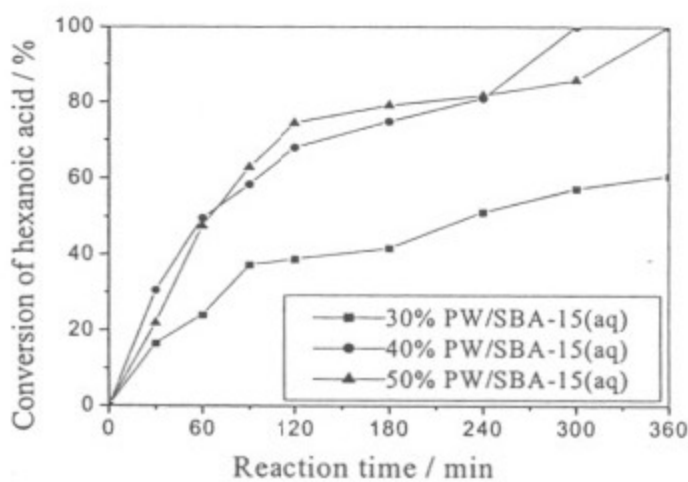


Fig. 5. Effect of HPA loadings on catalytic performance (SBA-15 support)

Table 2

Conversion of hexanoic acid over various PW supported catalysts
(loading: 40% PW reaction time: 3h)

	CMK-1	CMK-3	Activated Carbon
0.1M HCl	42.9	54.4	61.4
CH ₃ OH	33.7	36.8	58.4

commercial silica. As shown in Table 2, commercial activated carbon was a better carrier than mesoporous carbons when impregnated in methanol or HCl but aqueous impregnation resulted in poor conversion; the former having the larger surface area (ca. 1500 m²/g) than mesoporous carbons (ca. 1000 m²/g) and due to more hydrophobic nature of activated carbon.

Water or methanol was equally acceptable solvent for HPA for mesoporous carbon CMK-3, and this shows different surface nature of mesoporous carbons from commercial one. For acylation, again mesoporous materials produced better catalytic performance than commercial silica, and HPA on CMK-3 with larger pores performed slightly better than commercial carbon or CMK-1 (Fig.6 and Fig.7).

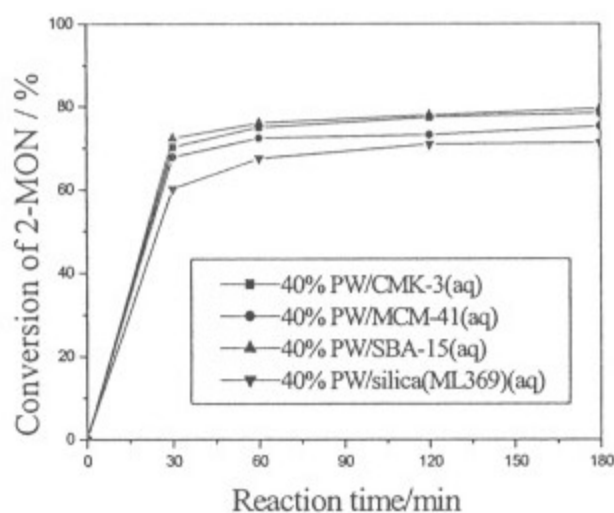


Fig. 6. Comparison of different supports on acylation activity

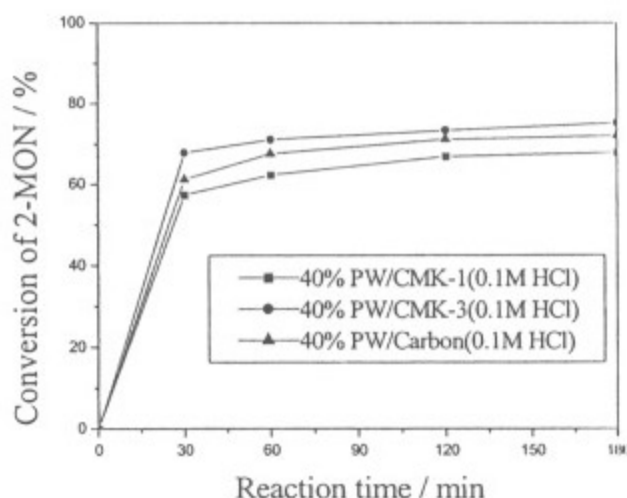


Fig. 7. Comparison of different carbon supports on acylation activity

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