



Direct synthesis, characterization and catalytic application of SBA-15 mesoporous silica with heteropolyacid incorporated into their framework



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ABSTRACT

The Keggin phosphotungstic acid, $H_3PW_{12}O_{40}$ (HPW) incorporated into SBA-15 ordered mesoporous silica were synthesized via a method involving the introduction of HPW in an acidified solution of P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$), the SBA-15 mesostructuring agent (direct synthesis). Samples with similar HPW loadings were also prepared by impregnation of SBA-15. A comparison between direct incorporation of HPW into mesoporous silica and impregnation of HPW on mesoporous silica was done. Characterization by elemental analysis, XRD, N_2 adsorption, TEM, DRS-UV and FTIR spectroscopy showed that after calcination HPW in the direct synthesized samples was better dispersed or may even be partially embedded in the pore walls. Moreover, their catalytic behaviors were investigated in the alkylation of *o*-xylene with styrene. Results show that direct synthesized sample has the better catalytic performances in terms of yield and stability. This behavior may be owing to high dispersion of the HPW species on the SBA-15 and the strong interaction between the HPW and the support, thus prevent HPW leaching from the support.

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1. Introduction

Heteropoly acids (HPA) have witnessed rapid growth in the last decade as solid acid catalyst [1–3]. Polyoxometalates with Keggin structure have been chosen as catalyst because of their easy availability and extreme stability in solution as well as in solid state. 12-Tungstophosphoric acid (HPW), in particular, has been the target catalyst among the Keggin series in many earlier reports because of the strongest acidity [4–5]. However, the main disadvantage is their very low surface area ($<10\text{ m}^2\text{ g}^{-1}$) and hence it becomes necessary to disperse HPW on supports that possess large surface area. The use of SBA-15 mesoporous molecular sieves is attractive, because it possesses well-ordered pore structures, high thermal stability and high surface area [6]. One possible route to obtain these supported HPW catalysts is the direct impregnation of the support with a heteropoly acid solution followed by evaporation of the solvent [7–9]. Although the conventional wet impregnation method is easy to increase its surface area by supporting HPW onto various carriers. However, weak interaction between the HPW and the support resulted in its leaching in polar media [10]. The reaction stabilities of the

catalysts are still not satisfactory. Thus, it is necessary to further improve the catalytic performances of the catalysts.

Leaching of HPW from ordered mesoporous silica in polar reaction media can be prevented by surface modification of the support. In our previous work, the deposition of basic alumina clusters; doping of the silicate with La atoms; and functionalization of the silicate walls with aminosilane groups for anchoring the HPW molecules were reported to be successful [11–13]. Incorporation of HPA into the pores of a mesoporous material can also be achieved by encapsulating HPA during the synthesis of the silica material itself [14–20]. Indeed, Yang et al. incorporated HPW into SBA-15 support by adding HPW to the SBA-15 synthesis mixture [15,17]. Toufaily et al. reported a similar approach to incorporate HPW into MSU type ordered mesoporous silica [18]. Shi et al. obtained SBA-15-supported HPW catalysts by adding P and W sources into the initial sol–gel system during hydrolysis of tetraethyl orthosilicate to form the Keggin-type HPA in situ [14,16].

In this work, The Keggin phosphotungstic acid (HPW) incorporated into SBA-15 ordered mesoporous silica were synthesized via a method involving the introduction of HPW in an acidified solution of P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$), the SBA-15 mesostructuring agent (direct synthesis). There are some important differences between other synthesis procedures and ours. The main difference is related to the timing of the introduction of HPW.

We introduced HPW before the hydrolysis of TEOS, whereas in References [15,17,18] TEOS was already present and had reacted

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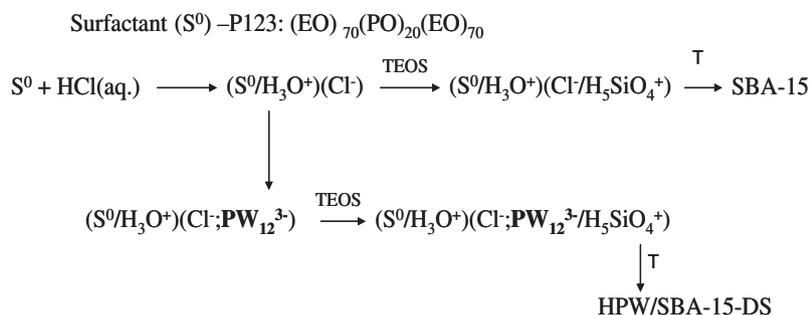


Fig. 1. Proposed synthesis mechanism for HPW/SBA-15-DS samples.

prior to HPW addition. Shi et al. introduced P and W sources (Na_2WO_4 and Na_2HPO_4) instead of HPW in the synthesis mixture.

The aim of this paper is to compare the differences between direct incorporation of HPW into mesoporous silica and impregnation of HPW on mesoporous silica. The effect of the incorporation/impregnation of HPW on the structure of mesoporous solids was investigated by different techniques. The catalytic properties of the catalysts were assessed in the alkylation of *o*-xylene with styrene. Special attention was paid to catalyst stability and reusability.

2. Experimental

2.1. Catalyst preparation

SBA-15 samples were synthesized following a previously published method using the P123 tri-block copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as a structure directing agent [6]. After the hydrothermal step, samples were thoroughly washed with distilled water and were dried at 120 °C for 24 h. Calcination was performed in air at 540 °C for 6 h (heating rate: 2 °C min^{-1}). The Keggin phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ -HPW) was dispersed on the silica support either using an aqueous incipient wetness impregnation technique or via a direct synthesis method.

The aqueous incipient wetness impregnation technique was previously employed by many authors for the immobilization and dispersion of HPA on high surface area supports [7–9]. We inserted 12-Tungstophosphoric Acid (HPW) by stirring 2 g of freshly calcined SBA-15 in a 10 mL aqueous solution containing 0.27 mmol of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ for 6 h at 353 K. The impregnated powders were dried at 120 °C overnight and calcined in air at 300 °C for 4 h. The resulting HPW/SBA-15 samples prepared via impregnation are denoted as HPW/SBA-15-PS (PS refers to the impregnation synthesis method).

Incorporation of HPW via the direct synthesis route was achieved via the following adaptation of the SBA-15 synthesis procedure (shown in Fig. 1). P123 polymer, 4.00 g; 30 g of water; and 120 g of HCl (2 M) were mixed following the standard method for SBA-15 synthesis. This solution was stirred for over 3 h at 40 °C and then added to a second solution containing 0.27 mmol of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ in a 10 mL aqueous solution. The mixture was stirred for 24 h before addition of 9.4 g tetraethyl orthosilicate (TEOS). During hydrolysis of TEOS a white precipitate was formed. After stirring for another 30 min, the mixture then transferred into a Teflon-lined autoclave and aged for 48 h at 80 °C. The resulting solid was filtered, washed with deionized water and dried at 100 °C for 24 h. The calcination step was performed in air at 540 °C for 6 h (heating rate: 2 °C min^{-1}). The resulting HPW/SBA-15 samples were labeled as HPW/SBA-15-DS (DS refers to the direct synthesis method).

2.2. Characterization

Elemental analysis of samples was performed by means of X-ray fluorescence (XRF) analysis on a SWITZERLAND ARL9800 XRF. The corresponding weight ratio of anhydrous HPW on dry SBA-15 of the different catalysts is exhibited in Table 1.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/max-rC Siemens diffractometer using nickel-filtered $\text{Cu K}\alpha$ as monochromatic X-ray radiation. The scattering intensities were measured over an angle range of $0.58 < 2\theta < 40$ with a step size $D(2\theta) = 0.028$ and a step time of 8 s.

The nitrogen adsorption and desorption isotherms were measured at –196 °C on an ASAP-2020 (Micromeritics USA). The specific surface area, A_{BET} , was determined from the linear part of the BET equation ($P/P_0 = 0.05\text{--}0.25$). The pore size distribution was derived from the desorption branch of the N_2 isotherm using the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of ca. 0.995. Pore structures of the samples were examined by TEM (Jeol, JEM-2000EXII).

Infrared spectra were recorded on a Bruker Tensor 27 (German) using DRIFT techniques, scanned from 4000 to 400 cm^{-1} . The sample was ground with KBr and pressed into a thin wafer. The samples were evacuated at 300 °C for 4 h before the measurement.

The diffuse reflectance UV–vis spectra were collected using a SHIMADZU UV3600 (Japan) scanning spectrophotometer. The powder sample was loaded into a quartz cell, and the spectra were collected over the range of 200–800 nm reference to BaSO_4 .

2.3. Catalytic tests

The alkylation reactions were carried out in a continuously stirred batch reactor under reflux conditions using a three-neck 100-mL round-bottom flask equipped with a condenser. Preliminary runs were conducted with 7.50 g (0.0721 mol) of styrene, 57.35 g (0.5402 mol) of *o*-xylene (mole ratio of *o*-xylene to styrene, 7.5:1) and 1.50 g of catalyst (20% w/w of styrene) at 120 °C for 180 min. The required amount of *o*-xylene was initially added to the reactor at the reaction temperature, followed by the desired amount of catalyst, a known amount of styrene was then added to the reaction mixture at the same temperature. After the reaction, unreacted *o*-xylene was distilled out under atmospheric pressure and then a collected part was called as crude product. The crude product was analyzed with GC-9890A gas chromatograph equipped with OV-1 capillary column and a flame ionization detector (FID). The yield of PXE was defined as follows:

$$\begin{aligned}
 \text{yield of PXE(\%)} &= \frac{\text{actual product weight}}{\text{all theoretical product weight}} \times 100 \\
 \text{actual product weight} &= \text{crude product weight} \\
 &\times \text{PXE(chromatography)\%}
 \end{aligned} \quad (1)$$

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