

Synthesis and Characterization of Heteropolyacid Functionalized SBA-15

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Abstract

12-tungstophosphoric acid (HPW), which possesses the strongest Brønsted acidity among heteropolyacids (HPAs), is a promising eco-friendly solid acid catalyst. However, its low surface area and inaccessible internal acid sites are the major drawbacks that limit its overall catalytic performances. While direct incorporation of HPW in ordered mesoporous silicas (OMCs) by conventional impregnation method helps to expose more acidic protons to reactants during reactions, such supported HPW/OMC systems tend to suffer from severe leaching and low recovery issues. In this context, immobilization of HPW on functionalized mesoporous silicas through chemical bonding should be highly desirable. Herein, the synthesis of HPW-functionalized SBA-15 is reported, their structural and acidic properties were characterized by a variety of different analytical/spectroscopic techniques.

Keywords: Functionalized SBA-15, heteropolyacids, Solid-state NMR, acidity, catalysis.

1. Introduction

As a potential candidate of eco-friendly heterogeneous acid catalysts, HPAs are known for their major disadvantages such as high solubility in polar solvents and low surface area. Immobilizations of HPAs on a variety of supports

[1-5] have been proposed to surmount such predicaments. Regarding to immobilization of HPW, the strongest Brønsted acidity among HPAs, inorganic substances such as ZrO₂, TiO₂, Al₂O₃, SiO₂, and carbons have been chosen as potential supports. Among them, silica supported HPW is known to possess superior stability and acidity [6], however, they are also drawback by severe leaching problem when a physical dispersion strategy was adopted. As such, chemical immobilization via chemical bonding between HPW and functionalized silica surfaces would be effective to expose sufficient acid sites while avoiding the leaching issue.

In this study, imidazolium rings were successfully grafted onto the pore surfaces of SBA-15 to immobilize HPW anions. The structural and physicochemical properties of HPW-IL-SBA-15 materials so prepared were characterized by a variety of analytical/spectroscopic techniques, such as N₂ adsorption-desorption isotherm, X-ray diffraction (XRD), and solid-state multi-nuclear NMR spectroscopy. Moreover, their acidic properties were also probed by using solid-state ³¹P MAS NMR of adsorbed trimethylphosphine (TMP) as the probe molecule [7,8].

2. Experimental

2.1 Catalyst preparation.

The synthesis was carried out by first preparing the ionic-liquid (IL) functionalized mesoporous SBA-15 using 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride,

which was synthesized from (3-chloropropyl)-trimethoxysilane and 1-methylimidazole (see Fig. 1a). In brief, a mixture of 4 mL of 1-methylimidazole and 9.3 mL of (3-chloropropyl)trimethoxysilane was microwaved for 1 h at 120 °C. The ionic liquid (**IL**) product was then transferred to a sample tube, then, purified by washing with ethyl acetate for five times. Subsequently, ca. 0.33 g of the **IL** was mixed with 0.50 g of SBA-15 in toluene (20 mL). The mixture was refluxed in a 100 mL, double-neck, round-bottom flask under N₂ atmosphere at 80 °C for 4 h. The obtained powders (**IL-SBA**) was collected by filtration, washed by deionized water and dried under 120 °C overnight.

Subsequent introduction of HPW invoked immobilization of the tungstophosphoric anions onto the positively charged imidazolium rings on the silica surfaces (see Fig. 1b). Typically, ca. 0.20 g of **IL-SBA** was added to a 30 mL acetonitrile solution containing 0.44g of HPW. The mixed solution was refluxed at 80 °C in a round-bottom flask under N₂ atmosphere for 24 h before it was filtered, washed and dried at 100 °C. Figures 1a and 1b are the schemes of the preparation procedures used in this study.

Various parameters involved during immobilization of HPW, such as surface coverage of **IL**, type of anions, and HPW loading, etc. were also examined.

2.2 Characterization.

All solid state NMR experiments were carried out on a Bruker AVANCE III 500 spectrometer using a 4-mm double-resonance MAS probehead. Powdered X-ray diffraction patterns were measured on a Philips X' Pert PRO X-ray diffractometer. N₂ adsorption-desorption isotherms of the porous substrate samples were measured on a Quantachrome Autosorb-1 volumetric adsorption analyzer. The surface areas and pore volumes of various samples were derived using the BET method.

3. Results and discussion

HSQC and HMBC spectra of **IL** are shown in Figs. 2 and 3, respectively. Peak assignments and correlations displayed in these spectra confirm the chemical structure of the prepared compound as **IL** (Fig. 1a).

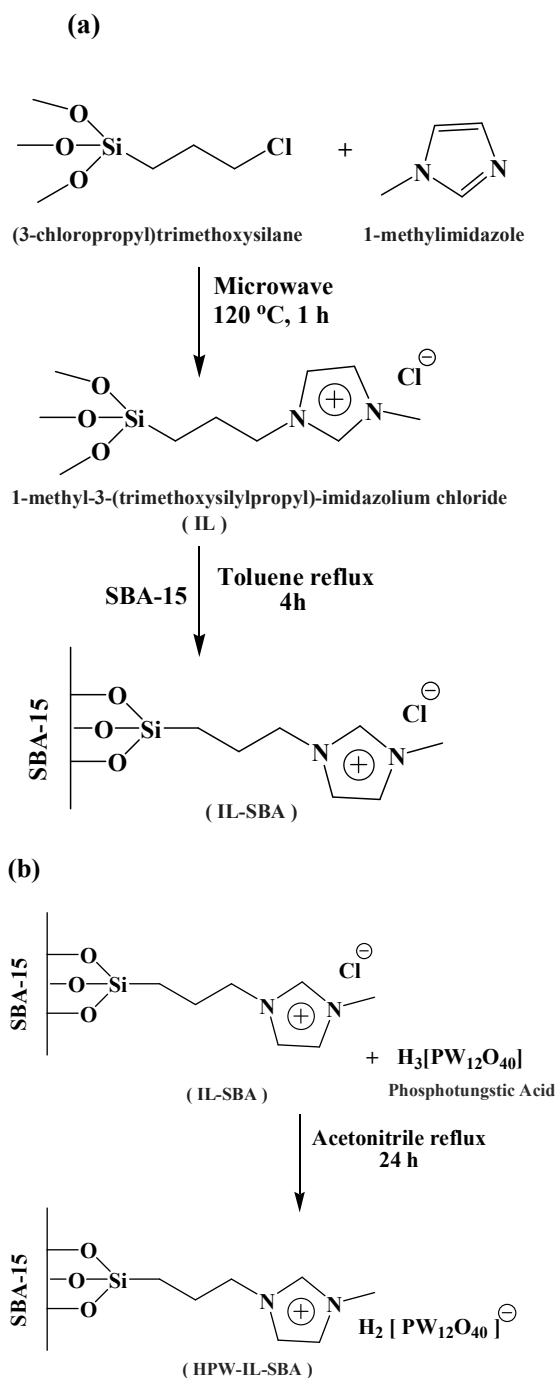


Fig. 1. Preparation of (a) **IL-SBA** and (b) **HPW-IL-SBA**.

As shown in Fig. 4, the ²⁹Si CP-MAS NMR spectrum of the **IL-SBA** revealed five peaks at ca. -109.7, -100.6, -91.5, -66.5 and -57.4. The peaks at ca. -109.7, -100.6 and -91.5 ppm arise from Q⁴ [Si(OSi)₄], Q³ [Si(OSi)₃OH] and Q² [Si(OSi)₂(OH)₂] sites of SBA-15, whereas the peak at ca. -66.5 and -57.4 ppm are associated with T³ [Si(OSi)₃C] and

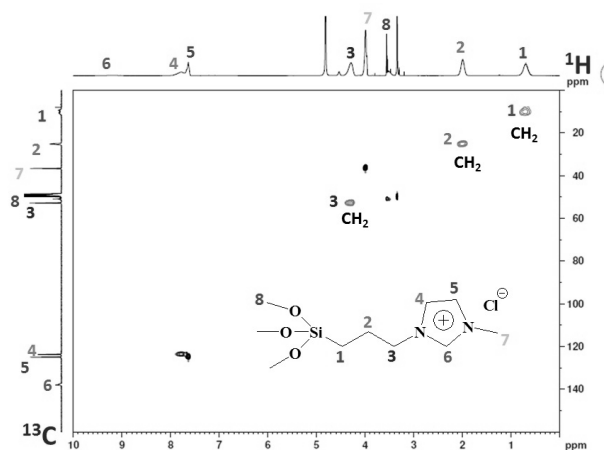


Fig. 2. 2D $\{^1\text{H}\}$ - ^{13}C HSQC spectrum of the IL.

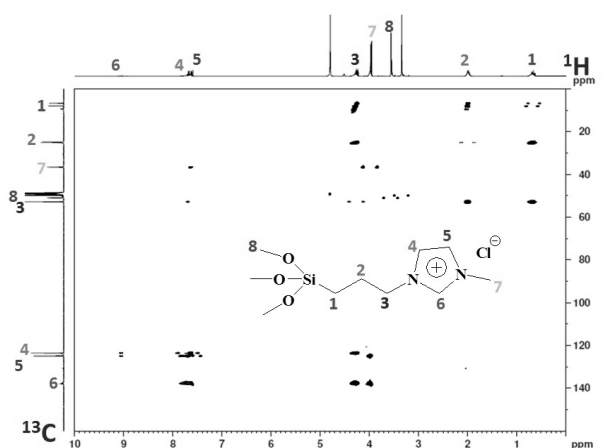


Fig. 3. 2D $\{^1\text{H}\}$ - ^{13}C HMBC spectrum of the IL.

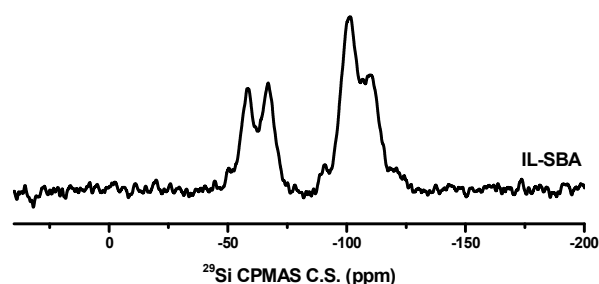


Fig. 4. ^{29}Si CP-MAS spectrum of IL-SBA.

T^2 $[\text{Si}(\text{OSi})_2\text{COH}]$ species. Moreover, the ^{13}C CP-MAS NMR spectrum of IL-SBA also revealed six peaks (Fig. 5), which can be unambiguously assigned to the six carbon atoms in the surface moiety of IL-SBA. Results obtained from both ^{29}Si and ^{13}C CP-MAS NMR confirmed that IL has been successfully grafted onto the pore surfaces. After immobilization of HPW onto the surface of IL-SBA, the six

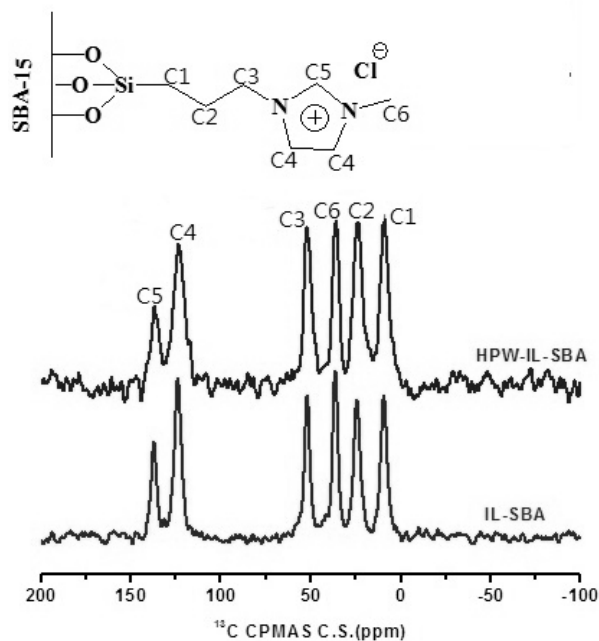


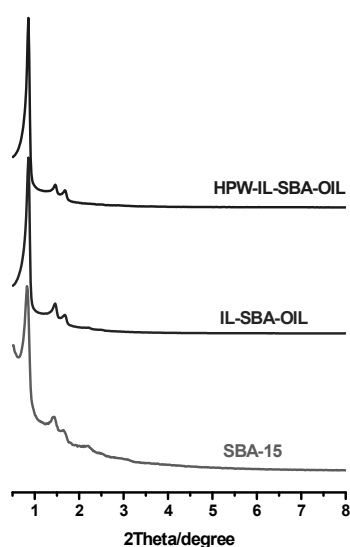
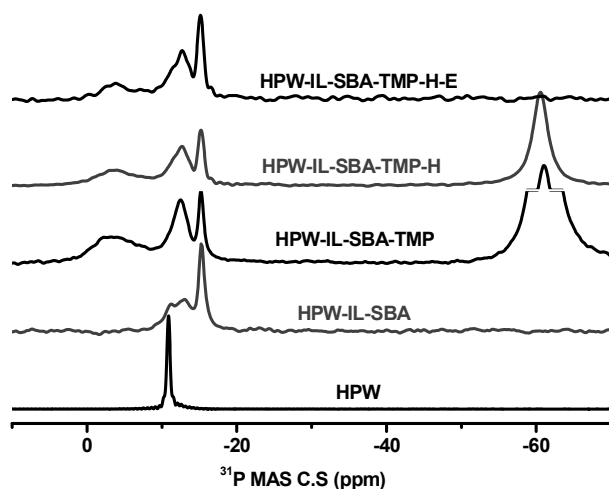
Fig. 5. ^{13}C CP-MAS NMR spectra of IL-SBA before and after loading HPW.

^{13}C resonances remain practically unchanged except that they are slightly broadened, reflecting the anchoring of HPW on IL-SBA-15 (which would eliminate the mobility of the nesting imidazolium ring [9]). The XRD patterns of SBA-15, IL-SBA, and HPW-IL-SBA samples (Fig. 6) all reveal characteristic diffraction patterns of mesoporous SBA-15. This indicates that the porous structure remains intact even after the functionalization and immobilization processes. The physical properties of various samples are summarized in Table 1. As expected, introduction of organic moieties and subsequent grafting of HPW onto the pore surfaces gradually decreases the surface area and pore volume. Nevertheless, the moderate decreases in pore surface area and pore volume upon incorporating the organic moieties and HPW, also indicate that they are indeed grafted on the pore surfaces and did not result in severe blocking of the mesoporous channels.

The base TMP was also used as the NMR probe to investigate the acidic properties of the HPW-IL-SBA samples, as shown in Fig. 7. For comparisons, the ^{31}P MAS NMR spectra of HPW and HPW-IL-SBA were also appended in Fig. 7. Typically, the adsorbed TMP give rise to two broad ^{31}P signals at ca. -4 and -60 ppm, which can be tentatively assigned to chemisorbed TMP on Brønsted acid

Table 1 Textural properties of various samples.

Sample	SBA-15	IL-SBA (IL 30%)	HPW-IL-SBA (HPW 20%; IL 30%)	IL-SBA (IL 10%)	HPW-IL-SBA (HPW 20%; IL 10%)
Surface area (m ² /g)	853	437	348	688	529
Pore volume (cc/g)	1.39	0.92	0.71	1.17	1.01

**Fig. 6.** XRD profiles of SBA-15 and IL-functionalized silica before and after loading HPW.**Fig. 7.** ³¹P MAS NMR spectra of HPW and HPW-IL-SBA before and after TMP adsorption and evacuation.

sites and physisorbed TMP, respectively. The latter peak diminished when the sample was subjected to heat treatment under vacuum at 80 °C, confirming the physisorbed nature of TMP. As such, the results obtained from ³¹P NMR of adsorbed TMP reveal that the HPW-IL-SBA sample indeed possesses accessible Brønsted acid sites on the surfaces of mesopores.

4. Summary

We have successfully immobilized HPW on the mesoporous SBA-15 by grafting imidazolium ring on the pore surface via an ionic liquid silane. Such SBA-15 supported HPW possesses the desirable mesoporous structure with accessible Brønsted acid sites on the pore surfaces. It is anticipated that such supported HPW-IL-SBA-15 is promising as a good heterogeneous acid catalyst for hydrocarbon conversions.

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