

Synthesis and Acidic Properties of Heteropolyacid Immobilized on Ionic Liquid-modified Mesoporous Silica SBA-15

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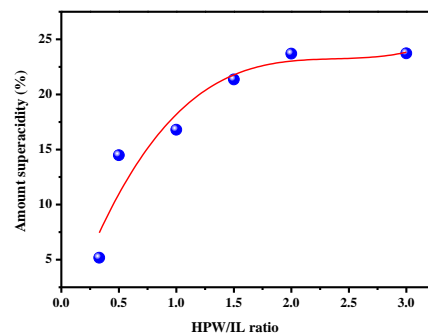
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12-tungstophosphoric acid (HPW), which possesses the strongest Brønsted acidity among heteropolyacids (HPAs), is a promising eco-friendly solid acid catalyst. However, its low surface area, inaccessible internal acid sites, and formidable separation/recycle issues are the major drawbacks that limit its overall catalytic performance. To overcome such drawbacks, an alternate approach is to disperse HPW on porous supports with high surface area, such as ordered mesoporous silicas SBA-15. In particular, it is desirable to anchor HPW on surface-functionalized supports containing amine moieties to render desirable catalytic activity and stability and to prevent leaching of the catalyst especially in the presence of polar solvents [1]. Herein, we report a novel route to prepare supported solid acid catalysts by immobilizing HPW on pyrrolic type ionic liquid (IL)-modified SBA-15 by impregnation method. The structure and textural properties of the HPW-IL-SBA-15 catalysts so synthesized were characterized by a variety of different analytical and spectroscopic techniques, such as EA, XRD, physisorption, FT-IR, and multinuclear solid-state NMR. Whereas their acidic properties were studied by solid-state ³¹P NMR of adsorbed trimethylphosphine oxide (TMPO); a technique which was developed by this laboratory [2].

It is found that the heteropolyanion retained its Keggin structure after anchoring onto the terminal pyrrolic nitrogen of the ionic liquid and subsequent washing treatment. In view of the presence of up to three protic sites on HPW [3], a careful control of its loading vs IL coverage on the surfaces of the silica support was made. On the basis of the ³¹P-TMPO NMR approach [2], the appearance of specific ³¹P resonance signals with chemical shift in the region of 86-93 ppm may be used as an indicator to verify the present of superacidity [3]. Indeed, our preprimary results reveal a consistent increase in amount of superacidity with increasing HPW/IL loading ratio, eventually reaching an anticipated plateau.

References:

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