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Acid catalyzed organic transformations by heteropoly tungstophosphoric acid supported on MCM-41

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ABSTRACT

In this work, solid acid catalysts of the Keggin-type 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) incorporated within the mesochannels of MCM-41 are prepared through a simple and effective impregnation method. The catalysts are characterized by various techniques such as XRD, FTIR, TEM, N_2 adsorption and thermal analysis. The surface acidities are measured by non-aqueous titration of *n*-butyl amine in acetonitrile and FTIR spectra of chemisorbed pyridine. The acidity and the textural parameters of the nanocomposites can be controlled simply by changing the loading of HPW on the MCM-41. The results indicate that the surface saturation coverage of MCM-41 is reached with 60 wt% HPW. The high saturation coverage is indicative of the well-dispersion of HPW within the mesochannels of MCM-41. The catalytic activities of the HPW/MCM-41 catalysts for the Pechmann, esterification reaction and Friedel–Crafts acylation reactions are studied in detail. Both the surface acidity and the catalytic activity sharply increase with the modification of MCM-41 by HPW. The sample with 60 wt% HPW shows the highest acidity and catalytic activity. The reusability tests of the catalysts show that the catalysts can be used several times without significant loss in activity. The HPW/MCM-41 catalysts have great potential for applications as commercial catalysts in promoting acid-catalyzed organic transformations under environmental friendly conditions and processes.

1. Introduction

In recent years, environmental considerations have raised strong interest in the development of economically feasible materials and processes to eliminate the use of harmful substances and the generation of toxic waste materials. In this respect, heterogeneous catalysis can play a key role in the development of environmentally benign processes particularly in the petroleum and chemical industries. For example, the substitution of liquid acid catalysts by efficient solid materials could contribute towards this goal. Highly porous molecular sieves such as MCM-41 provide an attractive possibility for the development of highly active solid acid catalysts [1,2]. MCM-41 is a promising support because of its large surface area (~1000 m^2/g), high thermal stability and large pore size (1.5–8 nm) [1–5]. However, MCM-41 lacks Brønsted acid sites and exhibits only weak hydrogen-bonded type of sites [6–8]. For MCM-41 to be used as a catalyst or catalyst support in acid-catalyzed reactions Brønsted acid sites need to be created and the acid strength must be enhanced. The acidity of MCM-41 can be increased by surface modification, through the introduction of strong acid species such as sulfate ions [9], sulfated zirconia [10] or heteropoly acids with Keggin-type structures [11,12], either on the surface or within the inner channels of MCM-41. This can result in creating Brønsted acid sites which can lead to a significant improvement in the acid strength of MCM-41.

Heteropoly solid acids with stable and strongly acidic properties, such as 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) have attracted much attention because of their strong acidity, high oxidation potential and redox characteristics which offer applications as Brønsted acid and redox catalysts [13–22]. Indeed, HPW supported on various materials has demonstrated high catalytic activity as an acid and oxidation catalyst for a variety for organic transformations including oxidative dehydrogenation of alkanes, olefin oxidation to epoxides, hydroisomerization and esterification reactions [13,16–18,23,24]. The choice of the support can overcome the major limitations of HPW which include low surface area of 5–10 m^2/g, low thermal stability and poor porosity [13–16]. For example, HPW clusters with diameters ~1.2 nm can be introduced inside the MCM-41 large pores of 2–8 nm, thus

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