



Metal-organic frameworks with high tungstophosphoric acid loading as heterogeneous acid catalysts



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ABSTRACT

High loadings of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) were incorporated within highly porous metal-organic framework MIL-101. The samples have been characterized using different techniques such as XRD, TEM, FT-IR, TGA, N_2 adsorption and Raman spectroscopy. XRD and TEM did not show any aggregation of the $H_3PW_{12}O_{40}$ nanocrystals on the surface of MIL-101 crystals up to 70 wt%. Similarly, N_2 sorption–desorption measurements reveal that samples with $H_3PW_{12}O_{40}$ loading up to 70 wt% retain their mesoporosity. The incorporation of $H_3PW_{12}O_{40}$ crystals gradually increases both the surface acidity and the acid strength of the $H_3PW_{12}O_{40}$ /MIL-101 catalysts up to 70 wt% loading. The catalytic performances of the $H_3PW_{12}O_{40}$ /MIL-101 solid catalysts were tested in three acid-catalyzed organic transformations, namely, the Pechmann, Esterification and Friedel–Crafts acylation reactions. In the three reactions, the catalytic activity attains the maximum value at 70 wt% of $H_3PW_{12}O_{40}$ loading, thus demonstrating direct correlation with dispersion, mesoporosity and acid strength. The unique attributes of MIL-101 and a well-dispersed level of $H_3PW_{12}O_{40}$ prohibit the conglomeration and deactivation of $H_3PW_{12}O_{40}$, which leads to the enhancement of the catalytic properties. The $H_3PW_{12}O_{40}$ catalysts supported on MIL-101 are potentially promising heterogeneous catalysts for acid-catalyzed organic transformations in environmental friendly processes, to supersede the use of conventional homogeneous $H_3PW_{12}O_{40}$ catalysts.

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1. Introduction

The development of active, environmentally benign and economically feasible heterogeneous catalysts is one of the important goals of catalysis research because of the urgent need to eliminate the use of harmful substances and the generation of toxic waste materials. For example, sulfuric and fluorohydric acids are commonly used in many industrial chemical processes that involve alkylation, esterification, hydrolysis, and other chemical reactions [1–4]. However, these acid catalysts are toxic, corrosive and most important, difficult to remove from the reaction medium. In this

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respect, the substitution of liquid acid catalysts with efficient solid materials could contribute to the green chemistry goal. This has raised strong interest in heteropoly solid acids such as 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) due to their strong acidity, stability, high oxidation potential and redox characteristics which offer applications as Brønsted acid and redox catalysts [5–14]. Unfortunately, pure HPW acids have very low surface areas ($5\text{--}10\text{ m}^2\text{ g}^{-1}$) and poor porosity which severely limits the accessibility of the active acid sites [5–8]. Therefore, it would be advantageous to incorporate the HPW acids within high surface area and highly porous supports. Indeed, HPW solid acids supported on a variety of high surface area and porous supports have demonstrated high catalytic activities as acid and oxidation catalysts for a variety of organic transformations [5,8–10,15,16]. The major limitations of some of these supports are the lack of well-defined and controlled structures and the low loading of the heteropoly acid crystals due to their tendency to aggregate on the surface of the support, thus leading to low catalytic activity.

Over the last decades, a class of highly porous crystalline supports has recently emerged from the field of metal-organic frameworks (MOFs) [17–21]. Versatile synthetic avenues with different combinations of organic linkers with metal ions allow for the design and synthesis of highly porous materials with control over pore metric and dimensionality that can be advantageous as catalyst supports. The mechanically robust walls of the frameworks can be used both to confine nanoparticle catalysts and to prevent their agglomeration. Although the use of MOFs in catalysis is a young research area, MOFs have been employed as solid catalysts or catalyst supports for a variety of applications [22–30]. A number of examples of the incorporation of heteropoly acids and polyoxometalates incorporated within or supported on MOF segments have been reported [31–37]. However, there is still a need to develop acid–base heterogeneous catalysts incorporated within the pores and channels of MOF systems. These catalyst systems could be realized by the incorporation of HPW nanocrystals within large pores of MIL-101, a chromium-based MOF with the molecular formula $\text{Cr}_3(\text{F},\text{OH})-(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})-\text{C}_6\text{H}_4-(\text{CO}_2)]_3 \cdot n\text{H}_2\text{O}$, $n \approx 25$ (MIL-101 for Materials of Institute Lavoisier) [34]. This porous solid is built from a hybrid supertetrahedral building unit formed by rigid terephthalate ligands and trimeric chromium (III) octahedral clusters. The resulting cell volume is about $702,000 \text{ \AA}^3$, with two types of cages with free diameters of 2.9 and 3.4 nm forming what is considered to be one of the most porous materials known to date [38]. The high surface area, mesoporous nature and stability in water could provide a highly effective host for solid acid catalysts. Ferey and co-workers have demonstrated immobilization of a Keggin heteropolytungstate within the cages of the MIL-101 [34]. However, some examples of catalysis over polyoxometalates-MIL-101 have been reported [34,39].

In this paper, we wish to report the synthesis of MIL-101 with different high loadings of the HPW nanocrystals incorporated within the large pores of MIL-101 through a simple impregnation method. The resulting catalyst materials were characterized by XRD, FT-IR, Raman, TEM, thermal analysis, N_2 adsorption, and non-aqueous titration. We also report the catalytic activity of these catalysts toward three different acid-catalyzed organic reactions under solvent-free conditions. We demonstrate applications of the prepared HPA-MIL-101 catalyst for three classes of acid-catalyzed reactions, and provide documentation of the stability of the catalyst and the effect of reaction parameters on conversion and product selectivity. The results suggest that highly efficient HPA catalysts supported on MIL-101 can be beneficial toward the development of environmentally benign processes in the chemical industry.

2. Experimental

2.1. Chemicals

Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$), chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%) and hydrofluoric acid (HF, 48%) were purchased from Sigma–Aldrich Chemicals. Terephthalic acid (98%) was purchased from Acros Chemicals. All chemicals were used without further purification. Nano pure water ($\sim 18 \text{ M}\Omega$) was used for all experiments.

2.2. Preparation of MIL-101

MIL-101 was synthesized and purified according to the method described by Kaskel [40]. Briefly, a clear solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (6.0 g), terephthalic acid (3.76 g), and hydrofluoric acid (0.75 ml) was prepared in 75 ml of H_2O and then introduced and sealed into a 250-ml Teflon-liner of a hydrothermal digestion bomb from Parr

Instruments. The mixture was then heated in a programmable oven (Isotemp, Fisher Scientific) to 220°C for 8 h with a ramping rate of $5^\circ\text{C}/\text{min}$. After cooling, the mixture was filtered to eliminate excess recrystallized terephthalic acid. The MIL-101 was activated hydrothermally in ethanol at 100°C for 4 h, then separated using a fine pore fritted glass filter. The solid was dried at 150°C , in air overnight to obtain MIL-101 crystals.

HPW was supported on MIL-101 by an impregnation method. 0.50 g of activated MIL-101 was added under vigorous stirring to a solution of the desired amount of HPW in 20 ml of distilled water for 24 h. After removing the water by evaporation, the sample was further dried at 110°C overnight in an oven and subsequently calcined at 275°C for 4 h in a muffle furnace. The color of the MIL-101 (pale green) did not change after the HPW loading. The prepared samples are abbreviated as $x \text{ HPW}/\text{MIL-101}$ (x varies from 50 to 90 wt% HPW).

2.3. Characterization

X-ray powder diffraction patterns of samples were determined using an X'Pert Philips Materials Research Diffractometer. The patterns were run with copper radiation ($\text{Cu K}\alpha$, $\lambda = 1.5405 \text{ \AA}$) with the second monochromator at 45 kV and 40 mA with a scanning speed of 2° in $2\theta/\text{min}$.

FT-IR spectra of calcined samples were recorded by using a Nicolet-Nexus 670 FT-IR spectrophotometer (4 cm^{-1} resolution and 32 scans) in dried KBr (Sigma) pellets and a measuring range of $400\text{--}4000 \text{ cm}^{-1}$.

The Raman spectra were measured using an excitation wavelength of 406.7 nm provided by a Coherent Saber DBW krypton ion laser. The laser beam was focused to a 0.2 mm diameter spot on the sample with a relatively low laser power of 0.07 mW. Higher laser powers resulted in noticeable sample degradation. The samples were pressed into a depression at the end of a 3 mm diameter stainless steel rod, held at a 30° angle in the path of the laser beam. The detector was a Princeton Instruments 1340×400 liquid nitrogen CCD detector, attached to a Spex (Horiba) model 1870 0.5 meter single spectrograph with a 1200 line/mm holographic grating (Jobin-Yvon/Horiba). The Raman scattered light was collected by a Canon 50 mm $f/0.95$ model 7S camera lens. Though the holographic gratings provided high discrimination, a Kaiser Optical holographic was used to provide additional filtering of reflected laser light, when necessary.

Transmission electron microscope (TEM) images and the particle size were obtained using a Jeol JEM-1230 operated at 120 kV. For TEM images the sample powder was dispersed in methanol by using ultrasonic radiation for 10 min, and a drop of the suspension was placed onto the carbon-coated copper grids.

The adsorption isotherms and the specific surface area (S_{BET}) of the various catalysts were determined from nitrogen adsorption studies conducted at -196°C using a Quantachrome Autosorb-1-C system.

The thermal stability of the samples was studied using TA thermal analyzers (DSC Q200 and TGA Q5000).

The total acidity of the solid samples was measured by means of potentiometric titration [41,42]. The solid (0.05 g) was suspended in acetonitrile (Merck), and agitated for 3 h. The suspension was then titrated with 0.05 N *n*-butylamine (Merck) in acetonitrile at 0.05 ml/min. The electrode potential variation was measured with an Orion 420 digital A model by using a double-junction electrode. Lewis and Brønsted acid sites present on the surface of the catalyst were determined with FT-IR spectra of adsorbed pyridine. Prior to the pyridine adsorption [42], small portions of the calcined samples were degassed under vacuum at 200°C for 3 h, followed by suspending in dry pyridine. The excess pyridine was removed by evaporation. The FT-IR spectra of the pyridine-adsorbed samples

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