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Polyoxometalates confined in the mesoporous cages of metal–organic framework MIL-100(Fe): Efficient heterogeneous catalysts for esterification and acetalization reactions

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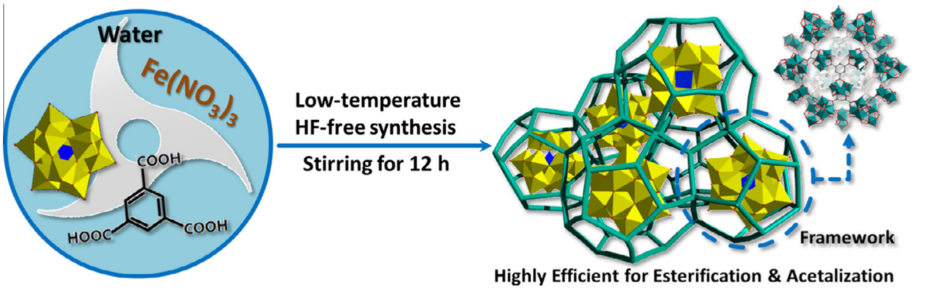
HIGHLIGHTS

- HPW@MIL-100(Fe) synthesized by a simple route under wild reaction conditions.
- HPW@MIL-100(Fe) shows high catalytic properties in acid-catalyzed organic reactions.
- HPW@MIL-100(Fe) is a promising candidate as solid acid catalyst.
- Synergistic effect between HPW and MIL-100(Fe) leads to the high activity of HPW@MIL-100(Fe).

GRAPHICAL ABSTRACT

The hybrid HPW@MIL-100(Fe) prepared by a simple low-temperature (<100 °C) HF-free incorporation route exhibits high catalytic properties in esterification and acetalization.



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ABSTRACT

12-Tungstophosphoric heteropolyacid (HPW) has been encapsulated in a mesoporous metal–organic framework (MOF), MIL-100(Fe), by a simple low-temperature (<100 °C) HF-free incorporation route via the reaction of ferric nitrate and trimesic acid in the presence of HPW. The resulting hybrid HPW@MIL-100(Fe) material was systemically characterized by XRD, N_2 adsorption, FT-IR, acid–base titration, ^{31}P MAS NMR, TEM, SEM, TGA, XPS techniques and elemental analysis, and then used as a heterogeneous catalyst in acid-catalyzed esterification and acetalization. The characterization results indicate that the HPW molecules were successfully incorporated within the mesoporous cages of the MIL-100(Fe) matrix as noncoordinating guests, thus maintaining the integrity of the protonic acidity of HPW. The resulting HPW@MIL-100(Fe) catalyst exhibits high activity and excellent reusability in the esterification reactions with no evidence for agglomeration, leaching, or deactivation of the HPW during several repeated uses of the catalyst. Similarly, the HPW@MIL-100(Fe) catalyst also shows excellent catalytic properties in the acetalization of benzaldehyde and ethanediol. The unique characteristics of MIL-100(Fe) and the uniform dispersion of HPW molecules within the mesoporous cages of the MIL-100(Fe) matrix may account for the high catalytic activity and recyclability of the HPW@MIL-100(Fe) catalyst.

1. Introduction

Metal–organic frameworks (MOFs) have attracted intensive interest due to their well-ordered crystalline structure, high

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porosity, large surface area, tunable pore size, and modifiable surface properties [1–3]. As an important class of advanced functional materials, MOFs have shown great potential in various research areas, such as gas adsorption/storage, separation, drug delivery, and heterogeneous catalysis [4–7]. Among the different classes of MOFs, some transition metal–organic frameworks exhibit relatively high hydrothermal and chemical stabilities [8–16]. These MOFs include mesoporous iron(III) carboxylate [MIL-100(Fe), with the chemical formula $Fe^{III}_3O(H_2O)_2(F \text{ or } OH)\{C_6H_3(CO_2)_3\}_2 \cdot nH_2O$ ($n \approx 14.5$)], which has a rigid zeotype crystal structure, consisting of 2.5 and 2.9 nm mesoporous cages accessible through window sizes of ca. 0.55 and 0.86 nm, respectively [16]. MIL-100(Fe) exhibits a very important porosity and a significant amount of accessible Lewis acid sites upon dehydration [16]. Besides its low toxicity and environmentally-friendly character, MIL-100(Fe) as a host matrix to support homogeneous catalyst possesses several unique characteristics including [16–21]: (i) high thermal (up to 280 °C in air) and hydrothermal stability, (ii) 3D mesoporous system allowing easy diffusion of the reactants, and (iii) low cost materials. Because of these excellent properties, MIL-100(Fe) has been applied in several different fields, including gas adsorption/separation, adsorption removal of heavy metal ions, dye, and N/S-heterocyclic contaminants, thin-film modifications, and heterogeneous catalysis [16–39].

Polyoxometalates (POMs) are a large family of anionic metal–oxygen clusters of early transition metals, and have attracted much attention as catalysts due to their strong acidity and excellent redox properties [40–42]. 12-Tungstophosphoric heteropolyacid (HPW), which has the strongest Brönsted acidity in the POMs series, shows promise as a solid–acid catalyst for many acid catalyzed organic transformations such as hydration, esterification, alkylation and hydrolysis [40–46]. However, bulk POM catalysts have low specific surface areas (typically $<10\ m^2\ g^{-1}$) and therefore, supporting POM catalysts onto high surface area materials is essential for successful applications in heterogeneous catalysis. Acidic or neutral support such as SiO_2, Al_2O_3, and activated carbon have been explored as POM carriers [47,48]. The acidity and catalytic activity of the supported POMs depend mainly on the type of support and on the extent of loading. For example, the strong interaction of POM molecules with activated carbon results in lower activity of the carbon-supported catalysts than that of bulk POM. On the other hand, weak catalyst-support interactions result in significant leaching of the POM molecules from the surface of the support. Encapsulation of POMs inside zeolitic cavities has been achieved by direct synthesis of the Keggin POM structures inside the super cages of the Y zeolite [49,50]. This approach is shown to solve the problem of leaching, since the POM clusters are larger than the windows of the zeolitic cavities, but only very low loadings can be achieved (<5 wt.%) which results in lower activity even if diffusion limitations could be avoided [49].

Supporting POM within the host space of MOFs, offers many advantages such as isolation of the Keggin units and simultaneously improving molecular accessibility as compared to bulk POM. The incorporation of the POM molecules within the MOF's matrix enables catalyst recovery by filtration and allows convenient reuse of the catalyst. MOFs-encapsulated POM clusters have been prepared either by impregnation or using a one-pot encapsulation method, especially with MIL-101(Cr) [another MOF having a similar structure with MIL-100(Fe)] as the host matrix due to its high thermal and chemical stabilities [51–67]. The one-pot encapsulation of Keggin POM into the cages of MIL-101(Cr) could offer some advantages over the impregnation method such as better dispersion of the POM molecules and more efficient utilization of the support [54–59]. However, most of the one-pot encapsulation methods of MIL-101(Cr) were carried out by hydrothermal syntheses under static conditions which result in several disadvantages such as the need for high temperature and long synthesis duration [56–67]. Another concern is the large mesoporous cages of MIL-101(Cr) (1.6 nm) which are too big to confine POM molecules (1.2 nm in diameter) [52–67], thus leading to a significant leaching of the catalyst in liquid phase reactions. However, in the case of MIL-100(Fe), the window sizes of its mesoporous cages (0.55 and 0.86 nm) are smaller than the diameter of the Keggin molecules [16]. Therefore, the leaching problem could be completely ruled out when the POMs molecules are encapsulated within the mesoporous cages of MIL-100(Fe). Unfortunately, the encapsulation of POMs in MIL-100(Fe) is still rarely reported [68], and no application of this hybrid material in the heterogeneous catalysis has been reported.

In our previous work, we successfully synthesized MIL-100(Fe) under HF-free conditions [39]. In this paper, we report the synthesis of the HPW@MIL-100(Fe) catalyst *via* a one-pot encapsulation method using a simple low-temperature (<100 °C) route at atmospheric pressure. Since the homogeneous catalysts in liquid phase acid-catalyzed reactions pose various disadvantages, such as toxicity, corrosiveness and tedious operation procedures, the use of heterogeneous catalysts is highly desirable [69–71]. Therefore, we then evaluated the catalytic properties of the prepared HPW@MIL-100(Fe) in the liquid phase esterification of acetic acid with monohydric alcohols [Scheme 1 in Supporting Information (SI)], as well as in the acetalization of benzaldehyde and ethanediol (Scheme 2 in SI). The results clearly demonstrate that the POM molecules can be incorporated within the mesoporous cages of the MIL-100(Fe) framework while maintaining the integrity of their protonic acidity thus imparting high catalytic activity and excellent reusability of the supported catalyst in the acid-catalyzed organic transformation reactions.

2. Experimental

2.1. Chemicals

All reagents with AR purity (analytical reagent grade) were purchased and used as received without further purification. Trimesic acid (H_3BTC), ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], HPW, ethanol, sodium hydroxide, *n*-butanol, *n*-hexanol, *n*-octanol, *n*-dodecanol, acetic acid, cyclohexane, benzaldehyde and ethanediol were purchased from Sinopharm Chemical Reagent Co. Ltd. An ultrastable Y zeolite (USY, Si/Al = 6) was supplied by Zhoucun Catalyst Factory. Deionized water with a resistance larger than 18.2 MΩ was obtained from Millipore Milli-Q ultrapure water purification system.

2.2. Catalyst preparation

MIL-100(Fe) encapsulated POM catalyst is prepared by a facile low-temperature (<100 °C) synthesis route at atmospheric pressure via reaction of trimesic acid, ferric nitrate and HPW under reflux. Typically, $Fe(NO_3)_3 \cdot 9H_2O$ (4.04 g, 10 mmol), H_3BTC (1.4 g, 6.67 mmol), HPW (0.5 g, 0.17 mmol), and deionized water (6 ml) were mixed and charged into a flask and then reacted at 95 °C for 12 h with vigorous stirring. The obtained orange solid was further purified by two-step processes using double solvent extraction with hot water and ethanol. For about 1 g hydrated solid, the solvent extraction has been performed using 60 ml water at 70 °C for 3 h and then 60 ml hot ethanol at 65 °C for 3 h. The solid was finally dried in a vacuum desiccator at 150 °C for 6 h prior to a further analysis or use. The resulting hybrid material was referred to as HPW@MIL-100(Fe). The bulk MIL-100(Fe) was also synthesized by the same method but without adding HPW in the starting synthesis system.