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Building MOF bottles around phosphotungstic acid ships: One-pot synthesis of bi-functional polyoxometalate-MIL-101 catalysts

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ABSTRACT

A new strategy has been developed for the direct encapsulation of polyoxometalates (POMs) into MIL-101(Cr). The addition of phosphotungstic acid (PTA) to the synthesis mixture of MIL-101 yields the direct encapsulation of chromium-containing polyoxometalates (POMs) inside the MOF structure, with a good distribution over the MIL-101 crystals. Vibrational Spectroscopy (DRIFT, Raman, UV–Vis) reveals the partial substitution of tungsten by Cr^{3+} resulting in the so-called lacunary structures, which are highly active in catalysis.

The medium-sized cavities of MIL-101 are occupied by POM units bigger than their pentagonal windows when this one-pot approach is followed, and no leaching is observed.

These new catalysts show the highest activities reported to date at 313 K for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate when using apolar toluene as solvent as well as when using polar DMF and ethanol, with TOFs exceeding 600 h^{-1}. In addition, they exhibit a remarkable activity in two acid-catalyzed reactions, the esterification of *n*-butanol with acetic acid in liquid phase slurry operation and the dimethyl ether production from methanol in a fixed bed gas phase operation, in contrast to the poor or absent activity of the catalysts prepared via the impregnation of the polyoxometalate in MIL-101, where the strong interaction between POM and support deteriorates the catalytic performance.

1. Introduction

Metal organic frameworks (MOFs) have attracted the attention of scientists all around the world during the last decades, resulting in an unprecedented explosion of publications in the topic. The combination of organic and inorganic subunits on fully crystalline porous materials has led to a vast chemical versatility, giving rise to more than 10000 MOF structures [1].

Considering the number of structures discovered, it must be realized that only a limited number of applications of these materials has been investigated. As reviewed very recently, research is focused mainly on the discovery of new structures [2–4] together with the characterization and identification of features like luminescence [5], or magnetic properties [6], while only a small percentage of the more than 1000 papers published every year on MOFs deal with specific applications. Among them, gas storage [7] and adsorptive separation [8,9] are the most studied.

Heterogeneous catalysis using MOFs is still in an immature state [10], being one of the most underdeveloped areas of the MOF research, as pointed out by Lee et al. [11]. Up to now, mainly proofs of principle related to catalysis on MOFs have been reported [12–18]. Serious catalytic studies, including long-term utilization and screening of different reaction conditions are still scarce [19–23]. This may be attributed to two main reasons. First the continuous *runaway* status of MOF chemistry is a strong driving force for proof of principle publishing, usually leading to incomplete works. Second, the use of MOFs in catalysis has been largely hampered by their relatively low thermal and chemical stability. In this sense, the MOF community is indebted to Ferey's group for discovering thermally and chemically robust structures [24–27]. The development of such structures provides an excellent playground for heterogeneous catalysis that has yet hardly been explored.

Indeed, materials like MIL-101 offer tremendous possibilities for catalyst engineering. This hybrid solid is built up from *supertetrahedra* (ST) building units, which are formed by rigid terephthalate ligands and trimeric chromium (III) octahedral clusters. The resulting solid owns two types of quasi-spherical mesoporous cages limited by 12 pentagonal faces for the smaller and by 16 faces for the larger. The so-called medium cavities are accessible through 1.2 nm pentagonal windows, while the large cavities are communicated through the same pentagonal windows and 1.5 nm hexagonal windows (Fig. 1) [24].

The presence of coordinatively unsaturated metal sites (CUS) in MIL-101 allows their use as a mild Lewis acid and, more importantly, allows their post-functionalization via grafting of active

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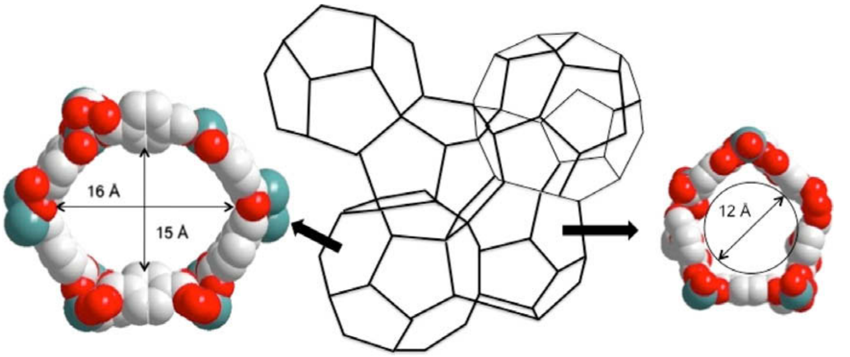

Fig. 1. MIL-101(Cr) structure. (Left) Hexagonal windows; (center) zeotype structure; and (right) pentagonal windows. Red: oxygen; green: chromium; and white: carbon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

species. In pioneering work, Jhung and coworkers demonstrated the possibility of post-functionalization of the MIL-101 framework with different amines and applied the obtained basic catalyst in a Knoevenagel condensation and for immobilizing metals [28]. The zeotype cavities of two different sizes, the fully accessible porosity, and therefore outstanding sorption properties, together with a high thermal and chemical stability make MIL-101 an excellent candidate for supporting catalytic species. In this sense mainly two post-synthetic approaches have been followed: the deposition of Pd nanoparticles for the use of MIL-101 in hydrogenation reactions [29] and the impregnation of polyoxometalate anions in the large cavities for their later use as an oxidation catalyst [21].

Polyoxometalates (POMs) present several advantages as catalysts that make them economically and environmentally attractive [30]. POMs are complex Brønsted acids that consist of heteropolyanions having metal-oxygen octahedra as the basic structural units. The first characterized and the best known of these is the Keggin heteropolyanion, typically represented by the formula $XM_{12}O_{40}^{x-8}$ where X is the central atom. With a very strong Brønsted acidity, approaching the superacid region, and exhibiting fast reversible multi-electron redox transformations under rather mild conditions, POMs represent a serious alternative to other acid systems. Their acid–base and redox properties can be varied over a wide range by changing the chemical composition. This unique structure exhibits extremely high proton mobility, while heteropolyanions can stabilize cationic organic intermediates. On top of that POMs have a good thermal stability in the solid state, far better than other strong acids like ion exchange resins [30].

Supporting POM catalysts is important for applications because bulk POMs have a low specific surface (1–5 m^2/g). Acidic or neutral substances such as SiO_2, Al_2O_3, and activated carbons have been explored as carriers [31–35]. The acidity and catalytic activity of the supported POMs depend mainly on the type of carrier and on the loading, i.e. the interaction with activated carbons is so strong that the activity of the final catalyst is much lower than that of the POM itself, while low interactions of POM–support lead to dramatic leaching. Encapsulation of POMs inside zeolitic cavities has been achieved by direct synthesis of the Keggin structures inside the zeolite cavities (FAU). This approach is shown to solve the problem of leaching, since the POM clusters are bigger than the windows of the zeolitic cavities, but only very low loadings can be utilized (<5 wt%) if diffusion limitations are to be avoided [36].

As explained before, polyoxometalates with the Keggin structure have been impregnated into the large cavities of MIL-101. Lacunary $PW_{11}O_{40}^{7-}$ anions (one tungsten less than Keggin ion) were introduced in order to demonstrate the large volume of such large cavities [24]. Following a similar approach, Maksimchuk et al. impregnated different Ti and Co Keggin anions into the large cavities of MIL-101 and the catalytic performance of the resulting materials was assessed in the oxidation of three representative alkenes using molecular oxygen and aqueous hydrogen peroxide as oxidants. The catalysts could be reused several times without significant activity losses and they were shown to be stable under mild operation conditions [21]. Very recently, a series of HPAs were encapsulated by means of a one-step hydrothermal reaction of copper nitrate, benzene 1,3,5 tricarboxylate (BTC), and different Keggin polyoxometalates. In these compounds, the catalytically active Keggin polyanions were alternately arrayed as noncoordinating guests in the cubo-octahedral cages of a Cu-BTC MOF host matrix (HKUST-1), showing activities similar to that of the bare acid in the hydrolysis of some esters, although diffusion limitations seem to be a problem in the case of CuBTC due to the comparable size of the Keggin anions and the large cavities of this MOF [18].

In the case of MIL-101, the impregnation approach has been demonstrated to be successful, but only the large cavities of MIL-101 can be accessed by Keggin-like structures (13–14 Å diameter). Taking into account that the medium-sized cavities represent 2/3 of the total number of cavities in MIL-101 and that the window openings of these cavities are smaller than those of the Keggin structures, it is obvious that the encapsulation of such active species into the medium cavities would offer many advantages, like a better dispersion and utilization of the support. Moreover, if contained in the medium cavities, leaching of the polyoxometalates would never be a problem, since they are bigger than the windows of these cavities.

In this work, we present a new, direct synthetic encapsulation of active species into MOFs [12,18]. We demonstrate that it is possible to incorporate highly dispersed POMs into MIL-101 by following a one-pot synthesis approach. Moreover, we show that the interaction of Cr^{3+} ions with phosphotungstic acid during the encapsulation process results in the stabilization of lacunary POMs due to the exchange of tungsten by Cr^{3+}. In addition to a complete characterization of the POM encapsulated samples, their catalytic performance is shown for reactions involving proton-abstraction (Knoevenagel), liquid phase acid-catalyzed esterification (acetic acid with *n*-butanol) and gas phase acid-catalyzed etherification (methanol dehydration).

2. Experimental

2.1. General information

All chemicals were obtained from Sigma–Aldrich and were used without further purification. High resolution transmission electron microscopy (HRTEM) on a Philips CM30T (150–300 kV) microscope