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MOFs meet monoliths: Hierarchical structuring metal organic framework catalysts

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ABSTRACT

Structuring heterogeneous catalysts from the micro- to the macro-level is essential for efficient catalyst utilization. The optimized synthesis and the catalytic performance of a Metal-Organic Framework, MIL-101(Cr), immobilized on a monolithic structure is presented. Secondary seeded growth is the optimal procedure to obtain uniform coatings of ~9 wt.% inside the monolith channels. A monolithic stirrer reactor has been used as playground for exploring reactivation procedures of MIL-101 for the selective oxidation of tetralin in the liquid phase. The presented results confirm the long-term stability of the catalyst, and the absence of any transport limitations in this reaction. The easy recovery of the catalyst allows performing as many reuses as necessary, something impossible to realize when working in the often-practised slurry operation mode. The reported results demonstrate that MIL-101(Cr) undergoes reversible deactivation attributed to the strong adsorption of products on the Cr sites. Applying the proper regeneration procedure (washing in chlorobenzene and air treatment @ 523 K) the initial performance is fully recovered.

1. Introduction

Metal Organic Frameworks (MOFs) have attracted the attention of scientists all around the world during the last decade, 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].

In spite of the many structures discovered, form the application viewpoint, and more specially in the field of heterogeneous catalysis, MOFs are still in an immature state [2], being one of the most underdeveloped areas of the MOF research, as pointed out by Lee *et al.* [3]. Up to now, mainly proofs of principle related to catalysis on MOFs have been reported [4–10]. Serious catalytic studies, including long term utilization and screening of different reaction conditions are still scarce [11–16]. To a large extent, progress has been hampered due to the lower chemical and mechanical stability of MOFs as compared to e.g. zeolites. In this sense, the immobilization of such materials onto structured supports is of the highest importance, not only for catalysis but also for other applications like gas storage[17–19], adsorbents for GC columns [20], drug delivery carriers[21–23], photocatalytic purposes [8] or continuous gas separation by means of membranes [17,24].

Up to now only little effort has been devoted to the immobilization of MOFs onto structured supports [25]. Thus, only few groups have reported on the direct growth of single metal-organic framework crystals on different modified surfaces [20–23]. MOF-5, Cu3(BTC)2 and Zn2(bdc)2(dabco) crystals were on alumina and silica supports [20–22], while Mn(HCO2)2 crystals were deposited on graphite discs modified with formate. MOF-5 and MIL-53(Fe) were deposited on self-assembled monolayers (SAMs) on gold sufaces. [26,27] The first publications on membrane synthesis and separation have been reported very recently [28,29]. Gascon et al. [30] manufactured dense coatings of HKUST-1 on α-alumina supports following a secondary growing approach. However, to the best of our knowledge no catalytic report on such systems has been published so far.

Herein, MIL-101(Cr) is used, which is hybrid solid built up from carboxylate moieties, benzene-1,4-dicarboxylate (bdc), and trimeric chromium(III) octahedral clusters which have removable terminal water molecules and therefore provide potential unsaturated metal sites in the structure which can be used either as catalytic sites themselves or anchoring sites of active species [31,32]. The resulting zeotype architecture is built by the connection of large hybrid supertetrahedra which further assemble with formation of very large mesopores. The cell volume are huge ca. 702.000 $Å^3$, and the smaller of the two types of quasispherical cages

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are delimited by 12 pentagonal faces, and the larger ones by 16 faces (12 pentagonal and four hexagonal). After removal of the guests, the accessible diameters are 29 and 34 Å for MIL-101. The as-prepared materials contain water and free carboxylic acid within the pores. Their evacuation prior to gas loading induces significant weight loss without any loss of crystallinity under the given thermal conditions. The mentioned properties make this material a potential candidate for catalytic applications [16,33].

In pioneering work, Kim *et at.* [34] have shown that MIL-101(Cr) may be a good catalyst for benzylic oxidation. Indeed, chromium-based catalytic systems have long been known to be highly active and selective catalysts [35,36]. In addition, Cr sites on mesoporous materials showed higher conversions than those on microporous supports due to more efficient mass transfer. In these regards, MIL-101, having abundant atomically distributed Cr(III) sites accessible to the reactants (after removal of terminal water molecules) and uniform mesopores, is a promising material for such catalytic application. Although Kim et al. demonstrated the proof of concept of the utilization of a MOF with open metal sites in oxidation reactions, still some drawbacks have to be overcome, *i.e.* catalysts recovery and regeneration. In this sense, we propose the immobilization of the catalyst on a structured support as solution and as platform for a more detailed study of the catalytic properties of MIL-101. Furthermore, the immobilization of MIL-101(Cr) on monoliths opens up the use of this catalyst in both batch and continuous reactor operation.

Here, we report an example of a Metal Organic Framework successfully immobilized on a structured support, *i.c.* a monolith. The easy recovery of the catalysts allows studying long term utilization on a single catalyst batch, and therefore regeneration can be studied in detail. In addition, the advantages of immobilization in terms of absence of attrition and diffusion limitations (and therefore better catalytic performance) are discussed.

2. Experimental

2.1. Materials

All the reagents were purchased from Sigma-Aldrich and were used as received without further purification. Polished asymmetric α-alumina discs (25 mm in diameter, 2 mm in thickness, top layer pore size 80 nm, and support layer pore size 150 nm) supplied by Pervatech were used as supports for the synthesis of MOF thin layers. The cylindrical cordierite monolithic substrates (2.5 cm of length and 1 cm of diameter, square channels with a cell density of 62 cells cm^{-2} (400 cpsi) and a wall thickness of 0.18 mm) were supplied by Corning Inc.

2.2. Characterization

The equipment used to do the spin coating was SPS Spin 150 Spincoater at 1500 rpm. The crystalline materials were analyzed by X-ray diffraction (XRD) using a Bruker- AXS D5005 with Cu Ka radiation. Scanning electron microscopy and energy dispersive spectroscopic mapping were done using a JEOL JSM-840 scanning electron microscope configured with secondary and backscattered electron detectors as well as an energy dispersive X-ray spectrometer. Thermogravimetric analysis was performed by means of a Mettler Toledo TGA/SDTA851e, under O_2 at heating rates of 10 K/min. A Quantachrome gas adsorption analyzer was used to measure the N_2 adsorption-desorption isotherms of the synthesized materials. The laser Raman spectra were obtained by using a Renishaw Raman imaging microscope, system 2000. The green (λ = 514 nm) polarized radiation of an argon-ion laser beam of 20 mW was used for excitation. A Leica DMLM optical microscope with a Leica PL floutar L500/5 objective lens was used to focus the beam on the sample. The Ramascope was calibrated using a silicon wafer.

2.3. MIL-101(Cr) seed synthesis

MIL-101 is synthesized from a mixture of 1.63 g chromium (III) nitrate, $Cr(NO_3)_3{\cdot}9H_2O$ (97%); 0.7 g terephthalic acid, C_6H_4-1,4-$(CO_2H)_2$ (97%); 0.20 g hydrofluoric acid, HF (40%) and different amounts of water, 20 g (standard conditions) and 1, 1.5, 2.5 times diluted, resulting 4 different samples. The mixture is heated under microwave irradiation for 2 h at 180 °C. The crystalline product is doubly filtered off using two glass filters with a pore size of 45 μm to remove the free terephtalic acid. Then a solvothermal treatment is sequentially performed using ethanol 95% at 80 °C for 24 hours. The resulting solid is soaked in 1 M of ammonium fluoride (NH_4F) solution at 70 °C for 24 hours and immediately filtered and washed with hot water. The solid is finally dried and stored at 150 °C

2.4. MIL-101(Cr) coated α-alumina discs

Two different procedures were applied to cover the discs with seeds, spin coating and dip coating. In both cases a dispersion of 100 mg of crystals (size of 150 nm) and 100 mL of ethanol were sonicated during 12 hours, needed to avoid agglomeration of particles. Ethanol was chosen as a solvent because its volatile character enables fast evaporation during the seeding procedures.

In spin coating ten drops of the suspension were placed on the disc before starting the spinning 1500 rpm for 1 min. The procedure was repeated five times for each disc.

For dip coating the substrate (disc) is immersed in the solution containing the seed material at a constant speed. Then it remains fully immersed and stays motionless afterwards the disc is raised at a constant speed. This procedure was repeated 10 times.

Once the discs were seeded, a secondary growth was performed in rotating autoclaves heated in a conventional oven for 8 h at 220 °C. The synthesis mixture contained 0.63 g chromium (III) nitrate, $Cr(NO_3)_3{\cdot}9H_2O$ (97%); 0.7 g terephthalic acid, C_6H_4-1,4-$(CO_2H)_2$ (97%); 0.20 g hydrofluoric acid, HF (40%) and 25 g water. The activation procedure was similar to the one described above.

2.5. MIL-101(Cr) coated monolith synthesis

Two different methods were followed indicated by procedure A and B.

Procedure A: A slightly acidified (pH = 5) suspension of 50% of water and 50% of α-alumina (particles size of ~0.1 micrometer) was prepared under continuous stirring. Then, the cordierite monoliths were immersed firstly in a NaOH (0.1 M) solution, followed by immersion in the α-alumina suspension [36]. After that the monoliths were flushed with under air (air knife) and dried under rotation at room temperature during 12 h. The alumina coated monoliths were calcined at 1000 °C for 4 h (heating rate 2 °C/min) and seeded with MIL-101(Cr) nanocrystals (150 nm size). Seeding was performed by immersing the monolith under stirring in a seeding suspension (1 wt% of MIL-101(Cr) crystals in ethanol) for 1 hour. After that, the monolith was taken out from the solution and dried under vacuum during another hour at room temperature. Then, the remaining solvent was removed via evaporation at 100 °C.

The secondary growth was performed in an autoclave under rotation for 8 h at 220 °C using the standard synthesis conditions and activation procedure.

Procedure B: In procedure B a mixture of α-alumina and MIL-101 nanoparticles was coated on the monolith following the procedure described before. In this case the calcination step was done at 400 °C in order to preserve the integrity if the MIL-101(Cr).