



Bifunctional iridium-(2-aminoterephthalate)-Zr-MOF chemoselective catalyst for the synthesis of secondary amines by one-pot three-step cascade reaction [☆]

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ABSTRACT

A simple and efficient method for the synthesis of N-alkyl amines via a cascade reaction (hydrogenation + reductive amination) using a new recyclable hybrid catalyst that combines the catalytic power of transition metal complexes with the architecture of metal organic frameworks (MOFs).

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1. Introduction

Iridium-transition metal complexes are successful homogeneous catalysts, and their heterogenization over a solid matrix leads to the formation of solid recyclable molecular catalysts with well-defined active centers. In this sense, much effort has been done to design and develop adequate supports and heterogenization approaches that preserve the properties of the homogeneous catalyst and also improve their behavior by a cooperative effect between the metal complex and the support [1]. Another approach to transform a soluble catalyst (transition metal complex) into solid heterogeneous catalyst involves the synthesis of hybrid organic-inorganic structured porous materials [2] and coordination polymers [3]. Metal organic frameworks (MOFs) are one type of coordination polymers in which metal nodes are connected by organic linkers through strong bonds, forming crystalline hybrid microporous materials with a tridimensional network. In the last years, porous metal organic frameworks (MOFs) have aroused great interest for their potential application in gas separation [4]

and storage [5,6], sensors, and catalysis [7]. The most remarkable features of these networks as catalysts are the easy recovery and reusability and structure-dependent catalysis [8]. However, recently networks have been shown present unique active site structures and adequate porosity for shape and size selectivity and for regio- and enantioselective reactions. Although several series of MOFs have shown unusual thermal and chemical stability, their use in catalysis and gas separations is still limited by the lack of functional and selective sites in the most stable MOF frameworks [9]. Among the possible routes to create functional networks, we can highlight the direct synthesis and post-synthetic functionalization (PSM) [10], grafting of active groups on the open metal sites [11], and encapsulation of active species [12].

In the present work, we have prepared by PSM, multisite MOF catalysts starting from amine-functionalized Zn-(IRMOF-3) [13] and stable Zr-based MOFs (UiO66-NH₂) [14]. These new materials can act as heterogeneous catalysts that combine the properties of soluble organometallic complexes with those of the MOF as support. The high stability of the Zr-MOF (UiO66-NH₂) compared with the IRMOF-3 is an incentive to use the former for heterogeneous catalysis.

One-pot type reactions, in which several steps are performed in the same reaction vessel, are of much interest to achieve more sustainable process [15] by avoiding intermediate separation and purification steps and minimizing energy consumption [16]. These transformations known as tandem, domino, or cascade reactions

[☆] This work describes the one-pot direct reductive amination of carbonyl compounds with nitroarenes using new stable iridium-(2-aminoterephthalate)-Zr-MOF catalyst prepared by post-functionalization, employing molecular hydrogen as the reductant.

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[17] have become an important area of research in organic chemistry [18,19]. Compounds containing a nitro group are of interest as building blocks for agrochemicals, dyes, pharmaceuticals, and ligands [20]. In particular, nitroarenes are one of the most readily available starting materials in organic synthesis since they can be produced from a range of aromatic starting materials [21]. One example is the hydrogenation of nitroarenes into anilines, and further transformation by alkylation, reductive alkylation, hydroamination, etc., to obtain their derivatives including heterocyclic compounds [22]. In the present work, we will show the preparation of stable Zr-MOF-Ir for the synthesis of mono N-alkyl amines through reductive amination of aldehydes with nitroarenes, in a three-step cascade reaction. The recycling of the catalytic materials has been studied and shows that Zr-MOF-Ir-catalysts are stable after multiple reuses.

2. Results and discussion

The starting materials for this study were IRMOF-3 [13] (used as reference catalyst) and UiO66-NH₂ [14], since the presence of NH₂ groups in the linker (2-aminoterephthalic acid) of the MOFs allows to functionalize the material by conventional reactions, and PSM-MOFs can be prepared according to the well-established procedures. IRMOF-3 consists of a Zn₄O tetrahedron connected with six carboxylates to give a three-dimensional cubic porous material (Zn₄O(BDC-NH₂)₃); it has been prepared, in the last years, by different groups [23,13a] with different textural properties. Rowsell et al., have synthesized IRMOF-3 solvothermally with BDC-NH₂ (BDC-NH₂ = 2-aminoterephthalic acid) and Zn(NO₃)₂·4H₂O in N,N-diethylformamide with a BET surface area of 2446 m² g⁻¹. Gascon et al. obtain a high BET surface area of 3130 m² g⁻¹ in the N₂ protection [23b]. When IRMOF-3 was synthesized by a “direct mixing” synthesis strategy at room temperature, samples with a BET surface area of 750 m² g⁻¹ were obtained [13b,24]. This last strategy, using dimethylformamide (DMF) as solvent, was employed in this work, also obtaining IRMOF-3 with 750 m² g⁻¹ BET surface area and pores of ~10 Å [13b]. Although the Zn(II)-based MOFs have many favorable aspects, their poor stability to moisture and protic solvents is likely to limit their applications. This prompted us to use here more stable, chemically resistant frameworks such as Zr(IV)-based MOFs [25]. UiO-66 (UiO for University of Oslo) consists of a Zr(IV)-carboxylate cluster Zr₆(μ₃-O)₄(μ₃-OH)₄(CO₂)₁₂, which works as the secondary building unit (SBU) for the framework. The UiO-66 [Zr₆O₄(OH)₄(BDC)₆] (BDC = 1,4-benzenedicarboxylate) shows high thermal stability due to the presence of an inner Zr₆O₄(OH)₄ core in which the triangular faces of the Zr₆-octahedron are alternatively capped with μ₃-O and μ₃-OH groups. Cohen and Lillerud independently discovered that the UiO-66 motif was very tolerant to functionalized ligands, allowing the synthesis of UiO-66 MOFs and the amino-functionalized UiO-66-NH₂ derivatives with the same topology [26]. IRMOF-3 materials were obtained starting from Zn(NO₃)₂·6H₂O and BDC-NH₂ in DMF at 105 °C (BET surface area = 750 m² g⁻¹) [13b]. UiO-66-NH₂ was prepared by mixing ZrCl₄ and BDC-NH₂ in DMF, crystallization at 120 °C for 12–24 h, and activation by DMF exchange with ethanol followed by drying under vacuum (BET surface area = surface area of 800 m² g⁻¹).

MOFs can easily be modified by post-synthesis treatments with the aim of introducing functional groups that can act or be transformed into catalytic active sites [27]. Chelating groups, which can coordinate with a transition metal, can easily be introduced in MOFs [28]. For instance, IRMOF-3 reacts with salicylaldehyde to form the iminophenol ligand which reacts with Au(III) and V(V) complexes to give active catalysts in the hydrogenation of butadiene and in the oxidation of cyclohexene [13b,29]. UiO66-

NH₂ has also been modified by reaction with salicylaldehyde (vacuum-phase post-synthetic modification) [30] and with anhydrides [31], acting as an acid–base type catalyst for cross-aldol condensation reactions [14c]. Here, we present the importance of selecting properly the starting MOF material to be used as support for the preparation of heterogenized catalysts.

IRMOF-3 and UiO-66-NH₂ were reacted with 6-((diisopropylamino)methyl)picolinaldehyde as has been previously reported [13b]. The starting MOF was suspended in CH₂Cl₂ and treated with the aldehyde (Scheme 1) at room temperature for 30 min for IRMOF-3 (to prevent the loss of crystallinity) and for 24–48 h for the highly stable UiO66-NH₂. The reaction was then stopped by repeated washings of the solid material with CH₂Cl₂ and drying under vacuum. The contact time of this reaction is important for IRMOF-3, since it was observed that for contact times longer than 30 min the material obtained shows low crystallinity. According to the elemental analysis of the products obtained, a level of functionalization of 2% and 5% of the total –NH₂ groups for IRMOF-3 and UiO-66-NH₂, respectively, was achieved without losing the framework integrity. Meanwhile, iridium complexation by the imino-pincer complex was almost quantitative. Increasing the degree of functionalization with imine for IRMOF-3 required longer contact times. Unfortunately, this caused a severe decrease in the crystallinity of the final material, as commented above. Since the consecutive iridium complexation is quantitative, a 3% functionalization of the imine allows introducing up to 1.4 wt% and 3 wt% of Ir in IRMOF-3 and UiO-66-NH₂, respectively. The values obtained here are typical values for metal loading in useful heterogenized catalysts. It appears then that the sterically demanding 6-((diisopropylamino)methyl)picolinaldehyde reacts preferentially at the surface and at the channel entrance, showing the characteristics of molecular sieves for MOFs.

Since the reaction is not complete, the FTIR spectra of the resulting samples (see Figs. S4 and S9 in Supplementary) are still dominated by the bands assigned to the parent groups and by the skeletal modes of the MOFs, mainly due to the presence of the organic aromatic ligands (i.e., bands at 1600–1585 cm⁻¹, 1500–1430 cm⁻¹ and 700 cm⁻¹). The carboxylate anion has two strongly coupled C–O bonds with bond strengths between C=O and C–O. Bands between 1650 and 1550 cm⁻¹ (s) correspond to asymmetrical stretching for the carboxylates, and the band near 1400 cm⁻¹ (w) corresponds to symmetrical stretching. The presence of functional groups from post-synthetic modification of the starting IRMOF-3 or UiO-66-NH₂ can be observed in the full spectral range, being the intensity proportional to the level of conversion. The fraction of PSM was determined by normalizing FTIR spectra to the band at 760 cm⁻¹, assigned to the C–C vibrational mode in aromatic compounds (this band is relatively little affected by ring substituents) [14b], and which does not overlap with other vibrational modes. These samples will be hereafter referred to as IRMOF-3-L and UiO66-NH₂-L. The final step to prepare the Ir(I)-containing materials, IRMOF-3-LIr, UiO66-NH₂-LIr, consisted in reacting a suitable iridium precursor, [IrCl(cod)]₂, or [Ir(cod)(THF)₂]BF₄ with the imine-modified material. The preparative procedure is summarized in Scheme 1, while a detailed description of each step is given in the experimental section. The reaction with the aldehyde modifies UiO-66-NH₂ without degradation of the framework, even after extended reaction times and conversions, as indicated by the XRD results (see Fig. 1).

The functionalization process was also studied, by ESI-MS analysis (see Supporting material) on digested samples of UiO-66-NH₂ and PSM-derivatives. Due to the stability of UiO-66 MOFs in acidic media, hydrofluoric acid (HF) was chosen to digest the materials, taking into account the high affinity of Zr for fluoride. The starting UiO-66-NH₂ was also digested and used as reference. The negative mode mass spectra obtained showed a base peak at *m/z* 180 that corresponds to H₂BDC-NH₂ (Fig. S15a, [H₂BDC-NH₂ + H]⁻). The

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