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Engineering of coordination polymers for shape selective alkylation of large aromatics and the role of defects

Ugo Ravon [a], Marie Savonnet [a], Sonia Aguado [a], Marcelo E. Domine [a], Erwann Janneau [b], David Farrusseng [a,*]

[a] *Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 Avenue Albert Einstein, F-69626 Villeurbanne, France*
[b] *Université Lyon 1, Laboratoire Multimatériaux et Interfaces, F-69622 Villeurbanne, France*

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ABSTRACT

For economic and environmental reasons, there is a strong incentive to replace of homogeneous by green and efficient heterogeneous processes in catalysis. The Friedel-Crafts alkylation of aromatics is a marking example. Numbers of homogeneous catalysts (such as HF, H_2SO_3, and $AlCl_3$) have been replaced by H-form zeolites. However, large pore zeolite can not accommodate bulk aromatic molecules and/or alkylating agents avoiding the reaction to take place within the porous network. Due to their larger pore size, metal-organic frameworks (MOFs) open the doors to the alkylation of very large poly-aromatic compounds. We report different approaches for the design of acid shape selective MOFs. The first refers to a "zeolite mimetic" approach. It deals with the design of porous Zn or Al based MOF exhibiting bridging –OH species (MOF-69, MIL-53 Al) like those found in zeolites [Si–O(H)–Al]. The second approach aims at synthesizing MOF materials having structural defects to generate active catalytic centers. Two different synthetic strategies were investigated, either by fast precipitation or by the partial substitution of dicarboxylic by mono-carboxylic acid linkers. Acid centers have been characterized by solid ^1H NMR and Diffuse Reflectance IR. The mono-alkylation of biphenyl with *tert*-BuCl is achieved with 100% of para-selectivity, well superior to H-MOR and H-BEA reference zeolites.

1. Introduction

MOF materials can be regarded as a "new" class of catalytic materials at the frontier between active 3D inorganic frameworks like zeolites and surface organo-metallic compounds taking into account their porous structure and their accessible metallic nanoclusters, respectively. The possible organization and functionalization of active sites on the nanoscale provides the basis to develop materials specifically adapted to catalytic challenges like complex chemo-, regio- or stereo-selectivity. Although the later properties are still rarely reported for MOFs, the rapidly increasing studies on these materials with different design clearly demonstrate the versatility of metal-organic frameworks for catalysis [1,2]. MOF materials exhibiting paddle–wheel type nodes [3] have shown Lewis type catalytic activities such as cyanosilylation [4], terpene isomerization [5], alkene hydrogenation [6,7] and alcohol aerobic oxidation [8,9]. In addition, the organic moiety can be functionalized by reactive centers such as chiral basic groups [10] or metallo complexes [11].

For economic and environmental reasons, there is a strong incentive to replace of homogeneous by green and efficient heterogeneous processes in Catalysis. The alkylation of aromatics also known as Friedel-Crafts reaction is a marking example. Olefins, different types of alcohols, and also alkyl- and aryl-chlorides are applied as alkylating agents on a wide range of large scale processes in industry [12]. Numbers of strong mineral acids (such as HF, H_2SO_3, among others) and also Lewis acids (such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, among others), commonly used as homogeneous catalysts for this reactions, have continuously been replaced by H-form zeolites [13]. Thus, the shape selective β-methylation of naphthalene with methanol over mordenite (0.64×0.70 nm) to produce mainly 2,6-dimethylnaphthalene is one of the major examples in acid catalysis [14]. The high selectivity to the β-mono-methylation and/or β-di-methylation is mainly due to the larger size of the 1- and 3-oriented products which strongly limits their diffusion through the porous systems of medium pore size zeolites. However, large pore zeolite can not accommodate bulky aromatic molecules and/or alkylating agents making the reaction impossible to take place within the porous network. Due to their larger pore size, metal-organic frameworks (MOFs) open the doors to the alkylation of very large poly-aromatic compounds. Recently, Horcajada et al. [15] have reported the catalytic activity of two different MIL-101 (Fe, Cr) for Friedel–Crafts benzylation. We have very recently shown in a short account that microporous zinc carboxylate frameworks show outstanding shape selectivity properties on similar alkylation type reactions [16].

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[*] Corresponding author. Tel.: +33 4 72 44 53 65; fax: +33 4 72 44 53 9.
E-mail address: david.farrusseng@ircelyon.univ-lyon1.fr (D. Farrusseng).

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The first objective of this work is to explore different strategies to develop MOF materials exhibiting M–OH Brønsted sites for catalytic alkylation. Two main routes are investigated. The first route deals with the selection of MOF materials for which –OH groups are part of the structure as those found in H-form of zeolites. This solution can therefore be regarded as a design by zeolite mimetic approach (Fig. 1). The two compounds MIL-53(Al) [17] and MOF-69C [18] discovered by Ferey and co-workers, have been selected for testing. Both of them have well structurally identified hydroxyl groups as indicated in their formulae Al(OH)(bdc) and $Zn_3(OH)_2(bdc)$, respectively. The compound MIL-53(Al) is built from infinite chains of corner-sharing $AlO_4(\mu_2\text{-}OH)_2$ while MOF-69C consists of chains of $ZnO_2(OH)_2$ tetrahedron and $ZnO_4(OH)_2$ octahedron and with μ_3-OH as bridging species. The second route aims at creating defaults in a MOF network leading to nodes that are coordinated to –OH terminal groups, instead to a linker as they should be in a perfect structure. Here also, two strategies have been investigated (Fig. 2). We have anticipated that a synthesis by very fast precipitation may lead to crystalline compounds for which a fraction of linkers are missing in the network while still maintaining a robust structure. The second strategy consists in synthesizing MOF materials from a mixture of poly-dentate and mono-dentate linkers which shall yield "defects" at the nodes which are adjacent to the mono-dentate linkers. Because, MOF-5 or IRMOF family materials do not contain –OH groups with respect to the pure crystalline structure, we have selected MOF-5 as parent material to create –OH species as structural defects.

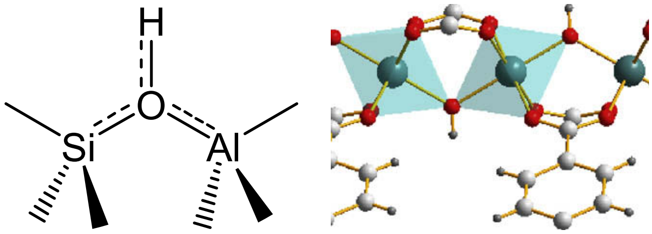

Fig. 1. MOF selection by zeolite mimetic approach. Scheme of Brønsted centers in zeolites showing μ_2 – bridging hydroxyl (left); Inorganic chain of MIL-53 showing μ_2 hydroxyl groups as potential acid centers (right).

A second objective is to address the properties of MOF for catalytic shape selectivity. Many metal-organic frameworks exhibit pore size and pore windows which exceed large pore zeolites such as beta (BEA) and mordenite (MOR). It is reasonable to envision that analogous shape selectivity effects can be also observed for MOF materials provided that the dimension of the micropores match well enough to discriminate between molecular sizes of different reagents, products or transition states involved in a particular process [19]. In this work, we have studied the alkylation of toluene and *tert*-butylbenzene, as well as larger aromatics such as naphthalene and biphenylene in order to better highlight pore-shape selectivity (Fig. 3). For the same reason, we reasoned that the *tert*-butyl group being much bulkier than the isopropyl usually studied, may be more suitable to observe larger degrees of shape selectivity. In this frame, the selection of IRMOF [20] and MOF-69 [21] materials were good candidates to investigate since their pore size can be tuned by selecting dicarboxylate ligands of different length.

2. Experimental

2.1. Synthesis

2.1.1. Solvothermal synthesis (MOF-5 solvo)

The synthesis of MOF-5 solvo was performed as reported by Sabo et al. [22]. Typically, 8.32 g (31.824 mmol) of $Zn(NO_3)_2{\cdot}4H_2O$ and 1.76 g (10.594 mmol) of 1,4-benzenedicarboxylic acid (H_2dbc) (Aldrich 99.7%), were dissolved in 100 ml of dried diethylformamide (DEF). The solution was heated at 100 °C in a Teflon-lined stainless-steel autoclave, the solid filtered off, washed and finally exchanged with $CHCl_3$ in argon flow. Finally, the material was evacuated and handled in a glove box for transferring in Schlenk type vessel.

2.1.2. Slow precipitation synthesis (MOF-5 basf)

The preparation of MOF-5 basf followed the procedure reported by Mueller et al. [23]. Typically, 3.22 g (10.8 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ (Riedel–Dehaën, pure) and 0.66 g (3.97 mmol) of H_2dbc were dissolved in 100 ml of DMF (Aldrich, 99.8% anhydrous and used as received). After 4 h of stirring at 130 °C, the solid was

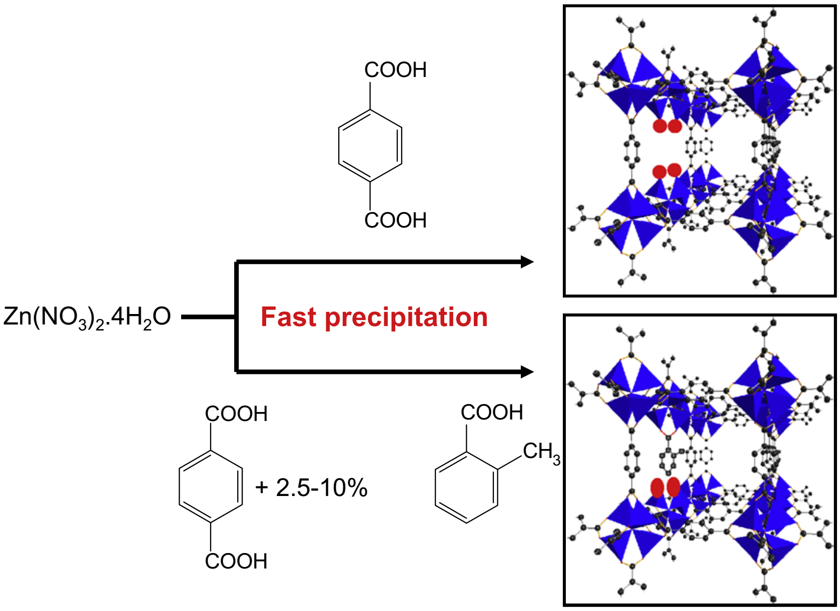

Fig. 2. Scheme of the two synthesis routes to generate structural defects; missing ligand (top), isomorphous substitution by a mono-carboxylic acid (bottom).