MOFs as acid catalysts with shape selectivity properties

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MOFs permit the paraalkylation of large polyaromatic compounds with nearly 100% of regioselectivity, offering new alternatives to standard zeolite catalysts.

Metal–organic frameworks (MOFs) are a class of crystalline hybrid material whose crystal structures are made up of extended 3D networks of metal ions or small discrete clusters connected through multidentate organic spacers.[1] The development of these porous coordination polymers has already opened up new perspectives in applications such as gas separation and storage.[2] The ability to tune pore size on an Angstrom scale while allowing the design of accessible metallic nanoclusters in a highly porous structure makes these compounds very attractive for catalysis.[3] The catalytic properties of HKUST-1, which uses Cu paddle wheel clusters as Lewis centres, is an outstanding proof of the concept.[4] However, we consider that published catalytic results are not in line with the generally acknowledged potential of MOFs. Indeed, only a limited number of successful catalytic studies have been reported.[5] Furthermore, the chosen catalytic reactions were usually model reactions of little industrial interest and/or reactions that did not need sophisticated catalysts in order to take place.

In contrast, the catalytic alkylation of aromatics is undertaken on a large scale in the chemical industry.[6] Among *para*-dialkylated aromatics, *para*-xylene, *para*-diisopropylbenzene, *para*-ethyltoluene, *para*-diethylbenzene, *para*- and *meta*-cymenes, and 4-*tert*-butyltoluene are very important in the fine chemical and petrochemical industries. Medium and large pore acidic zeolites are outstanding catalysts, since they combine high activity (acidic sites) and shape selectivity thanks to their micropore structures, which favour *para*-alkylation (less bulky products). Recently, the benzylation of toluene using the coordination polymer MIL-100(Fe) was reported.[7] However, shape selectivity properties were not investigated.

For the first time, we report herein MOFs that undertake an outstanding shape-selective alkylation of aromatics that outperform reference zeolites. The MOF catalysts are derived from well known IRMOF materials.[1c,3b] The cubic framework of IRMOF-1 consists of Zn_4O subunits that are linked in octahedral arrays of 1,4-benzenedicarboxylic acidic (BDC) groups to form a porous material with a channel window of about 8 Å. The topological simplicity of IRMOF-1 has lead to the preparation of a series of MOFs based on aromatic dicarboxylic acids coordinated to Zn_4O subunits. These structures, referred to as iso-reticular metal–organic frameworks (IRMOFs), have demonstrate that control over the pore size and functionality can be achieved. For instance, IRMOF-8 and IRMOF-10 are isoreticular compounds, with 2,6-naphthalenedicarboxylic acid (2,6-NDC) and 4,4′-biphenyldicarboxylic acid (4,4′-BPDC) as linkers, respectively.

The catalyst IRMOF-1 was prepared according to the method developed by Huang *et al.*, which consists of adding pure triethylamine to a solution of zinc nitrate and BDC in DMF.[8] This method was extended to the synthesis IRMOF-8 by using 2,6-NDC as the ligand.

Structural (X-ray diffraction, IR) and thermal (TDA, TGA) characterisation data for IRMOF-1 are in very good agreement with the results reported by Huang *et al.*[8] and Havizovic *et al.*[9] (Fig. 1 and Fig. 2). The sharp band at 3602 cm^{-1} can be assigned to Zn–OH species.[10] We also measured a 10% excess of Zn with respect to the theoretical formulae (elemental analysis and TGA), which leads to a global composition of $Zn_4O(BDC)\cdot 2H_2O + Zn(OH)_2$. According to Havizovic *et al.*,[9] zinc hydroxide nanoclusters that partly occupy the cavities are responsible for the structure distortion evidenced by the splitting of the diffraction peak at 9.7° (see inset to Fig. 1). On the other hand, the ^1H NMR spectra of different IRMOF-1 samples indicated the presence of Zn–OH–Zn species (very small peak at $\delta = -0.4$), like those encountered in $Zn_3(OH)_2(BDC)_2\cdot 2DEF$ (MOF-69c),[11,12] which contains

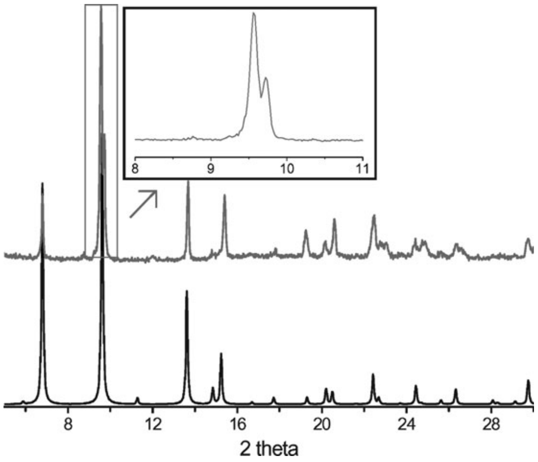

Fig. 1 Powder X-ray diffraction pattern of IRMOF-1: Top: Experimental result with zoom-in inset for the angles 8–11 (2θ). Bottom: Simulated pattern from MOF5-Zn.[9]

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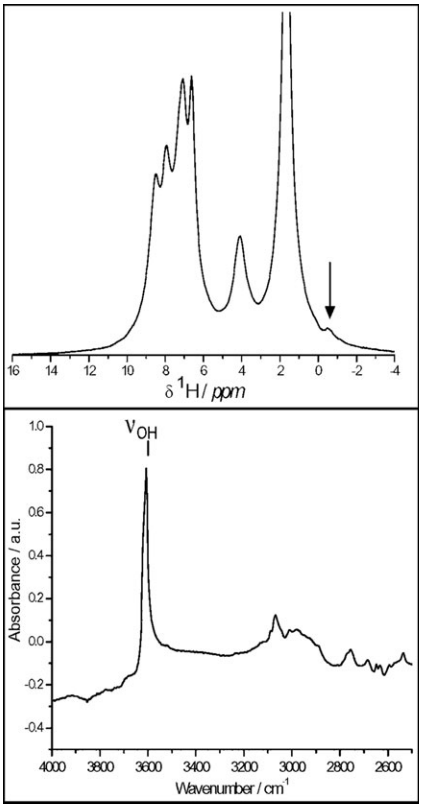

Fig. 2 IRMOF-1 short range characterization: Top: ^{1}H NMR. Bottom: *In situ* DRIFT after desorption at 220 °C.

Zn–(μ$_3$-OH)–Zn chains. Peak integration gave a ratio of one μ$_3$-OH for every 25 BDC linkers. The later phase can be formed during the synthesis of IRMOF-1, and is kinetically favoured in moisture conditions, as was the case in this study.[13] Therefore, in addition to zinc hydroxide clusters, IRMOF-1 samples also contain Zn–(μ$_3$-OH)–Zn chains in minor quantities, which could either be a crystalline default of the cubic structure or non-XRD detectable MOF-69c microcrystallites. Finally, it was recently demonstrated that pure IRMOF-1 undergoes a rapid phase transformation under moist conditions that is accompanied by a drastic decrease in accessible porous volume.[14]

From N_2 physisorption analysis at 77 K, the IRMOFs were determined to be microporous, and the isotherms were of type I. Their surface areas, micropore volumes and pore sizes correspond to those reported elsewhere that had similar preparation procedures to those used for IRMOF-1[8,9] and IRMOF-8 (Table 1).[15] A logarithmic plot (not shown) reveals that for IRMOF-8, N_2 adsorption occurs in two steps, revealing two distinct pore sizes. The actual calculation of the pore size using the Horvath–Kawazoe or Density Functional Theory (DFT) method is questionable, since the principal interaction potentials of the adsorbate and the adsorbent are unknown, and assumptions have to be made about pore morphology. The calculated pore diameters from the DFT method (Table 2) are therefore not fully accurate but, more importantly, allow comparison among members of a class of similar materials, which presumably have the same interaction potentials.

Table 1 N_2 physisorption results and comparison with literature data

Sample	Surface area/m^2 g^{-1} [a]	Pore volume/ cm^3 g^{-1}	Micropore volume/ cm^3 g^{-1} [b]	Pore diameter/Å [c]
IRMOF-1	450	0.32	0.18	8.8
IRMOF-8	730	0.46	0.29	7.3/11.6
H-BEA	430	0.62	0.10	7.7

[a] From BET analysis.[16] [b] From t-plot analysis. [c] From DFT analysis.

In order to complete the picture of the IRMOF samples with regard to their porosity properties, the calculated sizes of their cages and channel windows from the structural data of pure crystals are reported in Table 2. For example, the window between the cages of IRMOF-1 have a van der Waals space that can accommodate a sphere of approximately 7.8 Å diameter, herein referred to as the "free-space" diameter. In contrast to zeolite pore sizes, these values shall be interpreted with care for MOF materials, especially when correlating structural features and properties. Indeed, in addition to their general flexibility, the aromatic rings of IRMOF can rotate, thus making feasible the diffusion of larger guests.[1b,7,17]

Because of size matching between alkylbiphenyl compounds and large pore zeolites, the alkylation of biphenyl is an appropriate reaction to highlight the pore shape selectivity properties in acidic catalysis.[19] The activity and selectivity of the MOF samples were tested in the alkylation of toluene and biphenyl with *tert*-butylchloride in a batch reactor. The acidic form of beta zeolite (denoted hereafter H-BEA), $AlCl_3$ and $ZnCl_2$ were used as reference catalysts. As a result, IRMOF samples were as active as H-BEA and $AlCl_3$, and reactions were complete within 2 h at 170 °C (Table 3). For toluene alkylation, IRMOF samples exhibited a high selectivity for the less bulky *para*-oriented products, whereas $AlCl_3$ produced mixtures of *ortho* and *para* compounds. On the other hand, the alkylation of biphenyl revealed an exceptional selectivity for *para*-oriented 4-*tert*-butylbiphenyl with IRMOF samples. Indeed, only traces of dialkylated products (about 1%) were detected when using the IRMOFs. In contrast, H-BEA and $AlCl_3$ showed much higher selectivities for the *ortho*-oriented product, and about 15% for the dialkylated products. In conclusion, these results reveal the outstanding pore shape selectivity properties of IRMOFs for large polyaromatics.

Measurements of conversion at different reaction times indicate that there are similar kinetics for IRMOF-1, IRMOF-8 and H-BEA at 100 °C (Fig. 3). In contrast to MIL-101(Cr), IRMOFs are active in the first minutes of

Table 2 Theoretical cage and window sizes from structural data

	Cage free-space diameter/Å	Window free-space diameter/Å
IRMOF-1[a]	15.1	7.8
IRMOF-8[a]	18.0	9.2
H-BEA[b]	6.6	6.1

[a] Free-space diameter refers to the diameter of the largest sphere that can fit into the cage or through the window when the van der Waals radii from ref. 3*b* are assumed for all the framework atoms. [b] From ref. 18.

Table 3 Selectivity of *tert*-butylation reaction at 170 °C[a]

	Toluene			Biphenyl		
Catalyst	*para*[b]	*ortho*	di[d]	*para*[c]	*ortho*	di[d]
IRMOF-1	82	18	0	**96**	3	1
IRMOF-8	84	16	0	**95**	3	2
H-BEA	72	28	0	55	22	23
$AlCl_3$	46	54	0	51	38	11

[a] Conversions ranged from 60 to 80%. [b] *para-tert*-Butyltoluene. [c] 4-*tert*-Butylbiphenyl. [d] Sum of dialkylated products.

operation. These findings suggest that strong structural modifications are not required to create catalytic centers such as Zn–Cl[7]. Furthermore, the poor activity of $ZnCl_2$ tested as a powder at 170 °C (only 8% conversion) confirms that $ZnCl_2$ is not the catalytic specy.

After filtration, the catalysts could be re-used without any loss of activity or selectivity. XRD patterns of used IRMOF-1 did not show major modifications, whereas H^1 NMR revealed two significant changes (not shown). Firstly, integration of the broad peak at $\delta = 14$ revealed that about 20% of the carboxylate groups had been hydrolyzed to their acid form. Secondly, a very intense peak at $\delta = 3.4$ indicated the presence of a guest in the structure, which could be assigned as HCl. Indeed, very similar H^1 NMR spectra were obtained when concentrated HCl (36%) was added to fresh IRMOF-1. We suggest that the HCl, which is produced during the course of the reaction, is trapped in the framework, most likely at the oxygen containing nodes, provoking the partial hydrolysis of the host.

In order to check that the reaction takes place under heterogeneous conditions, issues of leaching were investigated. Firstly, tests in absence of solid catalysts were carried out under the same conditions, and any conversion was measured. Secondly, reaction mixtures were filtered-off after completion of the catalytic reactions, both solid catalyst and reaction solution being recovered separately. When a new reaction was started by adding fresh reactants to the recovered solution, any additional conversion was detected. This is consistent with the fact that HCl is trapped in the framework, making the filtrate HCl-free. Finally, we have observed that the reaction takes place at 50 °C with IRMOF-1. Under these conditions of pressure and temperature, the IRMOF samples were not soluble in decane, indicating that the reactions did not proceed in a homogeneous phase.

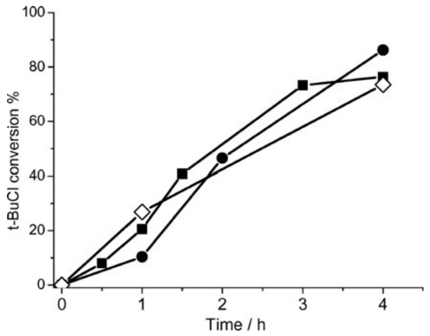

Fig. 3 Kinetic studies of toluene alkylation at 100 °C using IRMOF-1 (●), IRMOF-8 (■) and H-BEA (◇).

The exact catalytic centre is still unknown. As described earlier, acidic centres may arise either from zinc hydroxide clusters, from the presence of MOF-69c, or from structural Zn–OH defects formed at the synthesis step or upon water adsorption. Further experiments are ongoing in order to identify and assess these acidic sites.

From the experimental and theoretical data, there is, in principle, no steric hindrance to monoalkylated products diffusing out of the porous solids, including H-BEA. Even very bulky products, such as the dialkylated product 4,4′-di-*tert*-butylbiphenylene (12.5 × 5.0 Å), can be formed in large amounts in H-BEA.[19] Therefore, the shape selectivity properties observed for the IRMOF samples cannot arise from diffusion hindrance of the most bulky products, since the pore windows are even larger. For the reaction to take place, we suggest that the biphenyl is absorbed in a specific manner, allowing the formation of a transition state for the *para*-oriented product. Once alkylated, it can not be activated in the same manner because of steric hindrance, and double alkylation cannot proceed. Because of the porous structure similarities of IRMOF-1 and IRMOF-8, it is not surprising that similar selectivities are obtained.

In conclusion, we have demonstrated for the first time that MOFs can be used to undertake very shape-selective (almost 100%) catalytic alkylations of large molecules. This discovery may open new perspectives for the C–C coupling of polyaromatics or biomolecules that are too large to be addressed by zeolites.[20]

Saturation of the metal ion coordination sphere in coordination polymers is often argued to be a limitation of MOFs for catalytic applications.[21] We believe that the engineering of structural defects in MOF materials may lead to the generation of a new class of catalysts with different acidities and hydrophobic properties than are encountered in zeolites.

Original MOFs exhibiting M–OH functions and 100% regioselectivity have been recently discovered in our laboratory, and our findings will be published shortly. The investigation of other alkylating agents is also in progress.

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Experimental

Synthesis

All chemicals were used as received: DMF (Aldrich, 99.8%), $Zn(NO_3)_2{\cdot}6H_2O$ (Riedel-deHaën, pure), triethylamine (Riedel-deHaën, pure), BDC (Sigma Aldrich, 98%), 2,6-NDC (Alfa Aesar, 98%), $AlCl_3$ (Sigma-Aldrich, 99.99%) and anhydrous $ZnCl_2$ (Alfa Aesar). IRMOF-1 was prepared according to a procedure published by Huang *et al.*[8] A pure solution of 4.4 ml triethylamine (31.6 mmol) was added with stirring to a mixture of 660 mg (4.0 mmol) BDC and 2.4 mg (8.1 mmol) of $Zn(NO_3){\cdot}6H_2O$ dissolved in DMF. The white precipitate was recovered by filtration, washed with DMF and heated at 130 °C in air. H-BEA samples were obtained from Na-form (ENI Technology, Si/Al = 23 : 1) by ammonium exchange

(10 wt% NH_4COOCH_3 dissolved in water) at 80 °C for 4–5 h, followed by calcination at 550 °C for 3 h. This procedure was repeated twice.

Characterization

Samples were analyzed by X-ray diffraction (Bruker D5005), DRIFT (Magna 550 Nicolet, SpectraTech cell, ZnSe windows, MCT detector), N_2 absorption measurements (Micrometrics ASAP 2010 M) and chemical analysis (Spectroflame ICP-OES). IRMOF samples were further characterized by TG/TD analysis (Setaram-type SETSYS Evolution 12). For ^1H NMR (DX 400BRUCKER) MAS technique: 30 kHz spinning rate, pulse duration 3 μs and repetition time 16 s. Peaks: δ −0.4 (Zn–(μ_3-OH)–Zn), δ 1–3 (DMF), δ 4–5.5 (H_2O) and δ 6–10 (C_6H_6).

Catalytic alkylation

Toluene (Chimie-Plus, 99%), biphenyl (Alfa Aesar, 99%), decane (Alfa Aesar, 99%), *tert*-butylchloride (Alfa Aesar 98 + %) and mesitylene (Aldrich, 98%) were used as received. The reactants were dissolved in decane. The reaction was carried out with an aryl : *tert*-butylchloride ratio of 2 : 1. Typically, a mixture of 2 ml (18.8 mmol) of toluene, 1 ml of *tert*-butylchloride (9.2 mmol) and 7 ml of decane were placed in a 48 ml Teflon-lined autoclave (Top Industrie). 30 mg of catalysts were desorbed at 130 °C and 10^{-5} bar. After 2 h of stirring at 170 °C, the solid was recovered by room temperature filtration, and the filtrate was analysed by gas chromatography (HP 6890N equipped with a 30 m HP5 column), using 5% mesitylene as the internal standard.

Catalyst re-use and leaching tests

After the completion of reactions, the solid catalysts were first filtered off. The filtrate and recovered solid were then treated separately so as to investigate leaching issues and undertake reuse, respectively. Fresh reactants in the same ratio as those used in the previous tests were then added to the filtrate. The solution mixture (in absence of solid) was then heated to 170 °C for 2 h. Any conversion was then measured. On the other hand, the recovered solid was washed with water, ethanol and acetone prior to post-reaction characterization and reuse.

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