View Online

Solvent free base catalysis and transesterification over basic functionalised Metal-Organic Frameworks†

Marie Savonnet,[a,b] Sonia Aguado,[a] Ugo Ravon,[a] Delphine Bazer-Bachi,[b] Vincent Lecocq,[b] Nicolas Bats,[b] Catherine Pinel[a] and David Farrusseng*[a]

Received 7th June 2009, Accepted 31st July 2009
First published as an Advance Article on the web 18th August 2009
DOI: 10.1039/b915291c

Published on 18 August 2009 on http://pubs.rsc.org | doi:10.1039/B915291C
Downloaded by City College of New York on 22 November 2010

Metal-Organic Frameworks (post-)functionalised with nitrogen containing moieties undergo solvent free aza-Michael condensation and transesterification, surpassing molecular and functionalised MCM-type analogues.

Despite intensive efforts to develop new efficient, selective and recyclable solid base catalysts such as Layered Double Hydroxides (LDH),[1–3] hydrotalcite, KF and amino supported compounds, the development of green processes involving base catalysts remains a challenge.[4]

Thanks to their versatility, Metal-Organic Frameworks (MOF), which are at the frontier between zeolites and surface organometallic compounds, open new perspectives in heterogeneous catalysis.[4–6] In the context of base catalysis and the valorisation of large molecules, they possess two main assets: (i) a porous network which is usually large enough to accommodate molecules such as Fatty Acid Methyl Esters (FAMEs), and (ii) a degree of basicity and a hydrophilicity/hydrophobicity balance which can be tuned by (post)-functionalisation to adjust reactivities and adsorption properties, respectively. Direct functionalisation consists in selecting an already functional linker which is directly used in the synthesis through self-assembly, whereas post-functionalisation modifies the organic part of the solid by a chemical reaction which takes place within the porous framework. Amino-derived MOFs have been shown to be excellent platforms for the grafting of various synthons such as isocyanates and anhydride acids.[7,8,9,10]

The objective of this work is to explore functionalised MOF materials in an aim to perform transesterification of FAMEs and base catalysis in line with the principles of green catalysis.

Zinc carboxylate (IsoReticular Metal-Organic Framework IRMOF-3, **1a**) and triazolate ($ZnF(Am_2TAZ)$ (Am = amino, TAZ = triazolate), **2a**) were synthesised from aminoterephthalic acid using procedures described in ref. 11 and 12 and then tested in catalytic reactions. They both possess amino groups pointing to the channels which have pore openings of 7.4 and 4.6 Å for **1a** and **2a**, respectively (Fig. 1). Structural (X-ray diffraction, IR) and porous characterisation (N_2 physisorption at 77 K) results match with data reported in the literature (ESI†). Physisorption of CO_2 performed at 303 K, 1 atm reveals a threefold uptake (27.1 and 8.5 ml g^{-1}) for **1a** with respect to **2a**, which also corresponds to a much higher surface area for **1a** (S_{BET} = 623 m^2 g^{-1}).

In addition, both **1a** and **2a** were post-functionalised with pyridine groups in order to increase the hydrophobicity while maintaining a similar level of basicity (pK_a ~ 5 for aniline and pyridine). The grafting on solids **1a** and **2a** was performed by acylation with nicotinoyl chloride, yielding **1b** and **2b**, respectively (Fig. 1).

In a typical postsynthetic modification procedure, a suspension of **1a** (or **2a**) in DMF is treated with nicotinoyl chloride for 5 days at 100 °C, then filtered and washed three times with DMF to provide **1b** (or **2b**). Infrared analyses of **1a** and **1b** reveal a significant decrease in the two signals centred at 3500 and 3390 cm^{-1} corresponding to the stretching vibrational modes of $-NH_2$ species. The integration of these bands allows an estimation of ~50% functionalisation for IRMOF-3. The peak at 3070 cm^{-1},

[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.*
E-mail: david.farrusseng@ircelyon.univ-lyon1.fr
[b]*IFP-Lyon, BP 3, 69360, Solaize, France*

† Electronic supplementary information (ESI) available: Supplementary figures. See DOI: 10.1039/b915291c

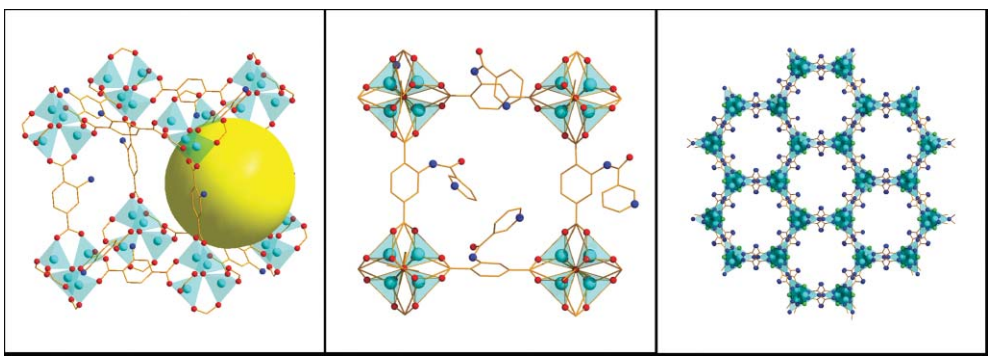


Fig. 1 Diagram of IRMOF-3 (left), functionalised IRMOF-3 (middle) and $ZnF(Am_2TAZ)$ (right) frameworks. The yellow balls indicate the size of the pore openings.

View Online

Published on 18 August 2009 on http://pubs.rsc.org | doi:10.1039/B915291C
Downloaded by City College of New York on 22 November 2010

assigned to νArC-H, reveals the presence of the nicotinoyl group, while the absence of a signal at 3600 cm^{-1} indicates that there are no Zn-OH bonds.[6] Further proofs of grafting are revealed by ^{1}H NMR and mass spectrometry (MS) analysis of digested **1b** in DCl/D_2O/DMSO-d_6. The negative mode MS clearly shows a base peak at m/z 285.1 ($M\text{-}H^-$) corresponding to the grafted linker. In addition, aromatic shifts of the grafted compounds were assigned by COSY experiments (^{1}H–^{1}H) (δ = 7.71, 7.82, 8.20, 8.36, 8.88, 9.20 and 12.16 ppm) (Fig. 2). The ^{1}H integration indicates a grafting rate of ~60%, which is close to that obtained *via* infrared measurements. Although the washing routine with DMF removes unreacted nicotinoyl chloride, 0.3 molecules per unit cage still remain in the porous network (Fig. 2). The decrease of the microporous surface from 650 $m^2\ g^{-1}$ for **1a** to 180 $m^2\ g^{-1}$ for **1b** confirms a reduction in free available space provoked by the introduction of basic groups and the presence of residual acid in the pore, which might be the cause of the loss of crystallinity.

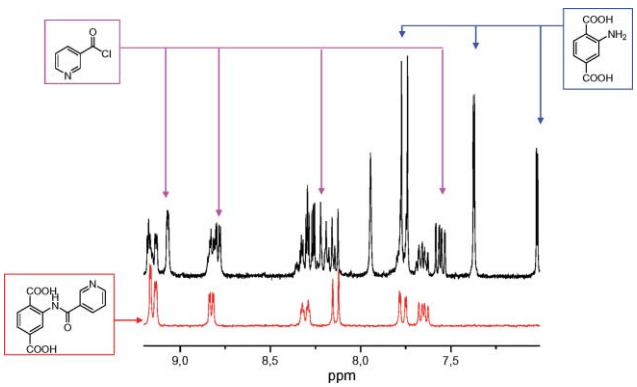


Fig. 2 ^{1}H-NMR of digested **1b** (top) and functionalised linker as reference (bottom).

In contrast, the crystallinity of the functionalised zinc triazolate (**2b**) is fully preserved. Unfortunately, the NMR quantification of the grafting rate cannot be performed on **2b** due to the absence of ^{1}H on the linker. A grafting rate of approximatively 60% was measured by elementary analysis based on the N and C contents. In addition, mass spectrometry analysis performed after digestion shows a signal at $m/z = 309$ corresponding to the doubly functionalised linker.

Catalytic materials were evaluated using aza-Michael reaction and simple transesterification as model reactions. Knoevenagel condensations are usually chosen as model reactions for evaluating base catalysts. However, the condensation liberates water which in our case could modify the structure of IRMOF-3.[13–15] In contrast, aza-Michael condensations do not liberate water and is appropriate to probe weak demanding base reactions. In addition, the aza-Michael reaction has found practical applications. The conjugate addition of amines to α,β-unsaturated compounds to form β-amino carbonyl compounds constitutes a key reaction in the synthesis of various complex natural products, antibiotics, β-amino alcohols and chiral auxillaries[16] (Fig. 3).

In an aim of probing the catalytic centres and getting rid of possible mass transfer limitations, ethyldecanoate was used as model compound for transesterification instead of bulkier triglycerides.

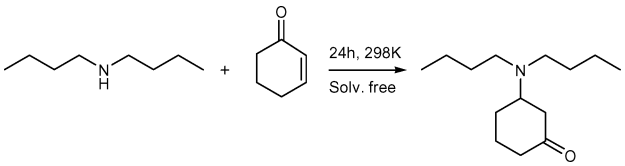


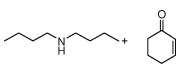
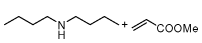
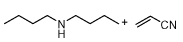
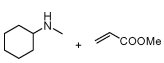
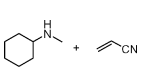
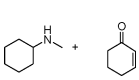
Fig. 3 Diagram of one example of the aza-Michael reaction. Reaction of dibutylamine with cyclohexen-1-one.

For comparison purposes, alkylamino-functionalised mesoporous ordered silica MCM-41 (Mobil Composition of Matter No.41)[17,18] (**3a**) and corresponding post-functionalised compounds[19] with 1.5% mol based on amino groups (**3b**) were prepared following the same procedure and then tested. Moreover, test reactions were carried out in homogeneous conditions with molecular analogues, namely aniline and pyridine which are the corresponding active centres for **1a**, **2a**, **3a** and **1b**, **2b**, **3b**, respectively.

Cyclic and acyclic aliphatic amines underwent 1,4-addition with different α,β-unsaturated compounds to afford the corresponding aza-Michael product without formation of byproduct (Table 1). The molecular catalysts *i.e.* aniline and pyridine show similar yields which is consistent with their very close pK_a, 4.6, and 5.2, respectively. Clearly, the functionalised MOF materials exhibit superior yields with regards to their molecular analogues and also with regards to MCM functionalised materials. Finally, highest yields are always found for post-functionalised materials **1b**, **2b** and **3b**, with respect to their parent forms **1a**, **2a** and **3a**. These self-consistent results point out the superiority of MOF catalysts over molecular and inorganic analogues. It has to be pointed out that the difference in yields according to the substrates results from the electrophilic character of the acceptor and the relative nucleophilicity of the donor. Highest yields are achieved for the most activated acceptor and/or the most nucleophilic donor.

For ethyldecanoate transesterification with MeOH (1:28), all MOF compounds reach 95% conversion after 24 h stirring at

Table 1 Catalytic results of aza-Michael reactions at room temperature based on 1.5 mol% on basic (aniline or pyridine type) groups and with a stoichiometry donor:acceptor of 1.0:1.1. The bold numbers indicate the highest yield obtained for each reaction.

	Yield (%)							
Substrates	Aniline	Pyridine	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**
	17	19	44	**47**	23	28	21	34
	66	70	76	77	59	**79**	63	65
	59	57	66	72	42	**85**	72	80
	82	83	90	**94**	88	90	84	86
	79	81	76	**94**	75	87	76	85
	19	22	24	29	20	**33**	18	24

 This journal is © The Royal Society of Chemistry 2009

View Online

180 °C (1.5 mol% catalyst), which corresponds to equilibrium. Catalytic runs were carried out at lower temperature (130 °C) in order to discriminate activities between the various MOFs (Fig. 4). Here again, **1a** and **1b** show the highest catalytic activities, with a significant enhancement of the yield after post-functionalisation with pyridine (TOF of 3 h^{-1}). On the other hand, for the MCM catalyst, a decrease in activity was observed after functionalisation (Fig. 4, **3b**). No further reaction takes place after removing the catalysts from reaction mixture, indicating the absence of leaching. After filtration, the MOF catalysts can be re-used twice without any loss of activity.

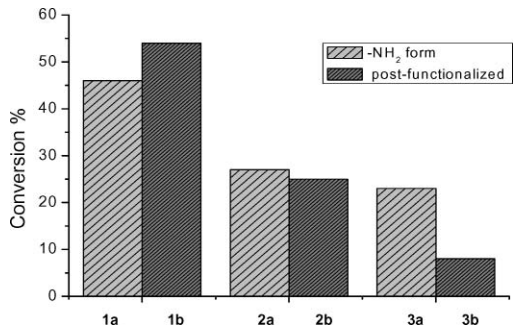


Fig. 4 Catalytic results of the transesterification of ethyldecanoate with MeOH (1:28) at 130 °C for 24 h.

The aza-Michael reaction does not require strong basic sites since it can proceed on pyridine polymers.[20] In contrast, stronger immobilized nitrogen bases such as guanidines are required for low temperature transesterification (*e.g.* 80 °C). However, weaker sites such as described herein are sufficient to perform the reaction in current process conditions (T = 190 °C, P ~ 30 bars).

We anticipate that the superiority of functionalised MOFs (**1b** and **2b**) against MCM analogue catalysts arises from the activation of the substrates *via* strong adsorption in the organic micropore framework whereas such confinement is not found in inorganic mesoporous MCM materials.

We report herein, for the first time, the application of functionalised Metal-Organic Frameworks to base catalysis. We believe that the development of post-functionalisation routes will make it possible to achieve tailor made materials that will create new breakthroughs in selective catalysis.

Experimental

Synthesis

All chemicals were used as received: *N*,*N*′-dimethylformamide, DMF (Aldrich, 99.8%), $Zn(NO_3)_2{\cdot}4H_2O$ (Merck, 98.5%), 2-aminoterephtalic acid (Alfa Aesar, 99%), nicotinoyl chloride hydrochloride (Aldrich, 97%), dichloromethane (Acros Organics, 99.99%), triethylamine (Riedel-de Haën, 99%), 4-(dimethylamino)pyridine DMAP (Aldrich, 99%), $ZnF_2{\cdot}4H_2O$ (Alfa Aesar, 98%), 3,5-diamino-1,2,4-triazole (Alfa Aesar, 98+%).

IRMOF-3 was prepared according to the procedure reported by Huang *et al.*:[11] 4.4 mL (31.6 mmol) of triethylamine was directly added to a DMF solution (80 mL) containing 2.4 g (8 mmol) of $Zn(NO_3)_2{\cdot}4H_2O$ and 0.66 g (4 mmol) of 2-aminoterephthalic acid under stirring at room temperature for 90 min. The powder was collected by repeated centrifugation and thorough DMF washing for three times. Then, they were dried at 130 °C under static air.[11]

$ZnF(Am_2TAZ)$ was prepared by placing a mixture of 0.2 g (2 mmol) of 3,5-diamino-1,2,4-triazole, 0.35 g (2 mmol) of $ZnF_2{\cdot}4H_2O$ and 10 mL of water into a 40 mL Teflon® lined autoclave. The resulting mixture was stirred for 5 min prior to sealing the autoclave. The autoclave was then placed in an oven and heated to 160 °C for 3.5 days.[12]

(Post-)functionalisation

All experiments were carried out under an inert atmosphere.

A sample of IRMOF-3 (0.85 g) activated at 250 °C for 12 h was suspended in dry, freshly distilled DMF and treated with one equivalent of nicotinoyl chloride (0.35 g) in the presence of an excess of distilled pyridine (5 mL) and DMAP (0.1 g) at 100 °C for five days. The resulting powder was collected by filtration, then thoroughly washed three times with DMF and dried under vacuum at 170 °C for 12 h. The same procedure was performed for the post-functionalisation of $ZnF(Am_2TAZ)$ and MCM-41-NH_2.

Catalytic reactions

Ethyldecanoate (Fluka, 99%), dibutylamine (Fluka, 99%), *N*-methylcyclohexylamine (Aldrich, 99%), methyl acrylate (aldrich, 99%), acrylonitrile (Aldrich, 99%), cyclohexen-1-one (Fluka, 98%), methanol (Aldrich, 99%), toluene (Chimie-Plus, 99%) and decane (Alfa Aesar, 99%) were used as received.

Aza-Michael reaction. The reaction of the donor group (5 mmol) with the acceptor group (5.5 mmol) in the presence of 1.5 mol% of catalyst based on the amino group was carried out at room temperature for 24 h.[3] After the reaction was completed and the catalyst filtered off, a sample of the filtrate was diluted in *n*-decane with 5% toluene as internal standard and analysed by gas chromatography (HP 6890 N equipped with a 30 m HP5 column).

Transesterification. Ethyldecanoate (2.5 mL) and methanol (10 mL) along with 1.5 mol% catalyst based on basic (amino or aniline) groups were made to react in a Teflon® lined stainless steel digestion bomb (TopIndustrie) for 24 h at 180 °C or 130 °C. After the reaction, the catalyst was recovered by filtration and a sample of the filtrate was diluted in CH_2Cl_2 and analysed by GC.

Acknowledgements

We thank Dr. A. Galarneau and M. F. Driole of the Institut Charles Gerhardt of Montpellier (France) for having provided us MCM-41 materials. We also thank A. Camarata and Dr. J. Pawlesa for the technical work, along with IRCELYON Scientific Services.

References

1 M. L. Kantam, A. Ravindra, C. V. Reddy, B. Sreedhar and B. M. Choudary, *Adv. Synth. Catal.*, 2006, **348**, 569–578.
2 V. P. Raje, R. P. Bhat and S. D. Samant, *Synlett*, 2006, **16**, 2676–2678.

Published on 18 August 2009 on http://pubs.rsc.org | doi:10.1039/B915291C
Downloaded by City College of New York on 22 November 2010

View Online

3 M. L. Kantam, B. Neelima and C. V. Reddy, *J. Mol. Catal. A: Chem.*, 2005, **241**, 147–150.
4 D. Farrusseng and C. Mirodatos, in *Design of Heterogeneous Catalysts*, U. S. Ozkan, (Ed.), Wiley-VCH, 2009.
5 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191–214.
6 U. Ravon, M. E. Domine, C. Gaudillere, A. Desmartin-Chomel and D. Farrusseng, *New J. Chem.*, 2008, **32**, 937–940.
7 Z. Q. Wang and S. M. Cohen, *Angew. Chem., Int. Ed.*, 2008, **47**, 4699–4702.
8 P. Gamez, J. S. Costa, C. A. Black, O. Roubeau, S. J. Teat and J. Reedijk, *Eur. J. Inorg,. Chem.*, 2008, 1551–1554.
9 S. Cohen, E. M. Dugan, Z. Q. Wang, M. Okamura and A. Medina, *Chem. Commun.*, 2008, 3366–3368.
10 M. J. Rosseinsky, M. J. Ingleson, J. P. Barrio, J. B. Guilbaud and Y. Z. Khimyak, *Chem. Commun.*, 2008, 2680–2682.
11 L. M. Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun, D. Y. Zhao and Y. S. Yan, *Microporous Mesoporous Mater.*, 2003, **58**, 105–114.
12 A. M. Goforth, C.-Y. Su, R. Hipp, R. B. Macquart, M. D. Smith and H.-C. zur Loye, *J. Solid State Chem.*, 2005, **178**, 2518.
13 S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Solid State Chem.*, 2007, **129**, 14176.
14 S. Hausdorf, F. Baitalow, J. Seidel and F. Mertens, *J. Phys. Chem. A*, 2007, **111**, 4259–4266.
15 S. Hausdorf, J. Wagler, R. Mossig and F. Mertens, *J. Phys. Chem. A*, 2008, **112**, 7567–7576.
16 M. E. Jung, B. M. Trost and I. Fleming, *Comp. Org. Synth.*, 1991, **4**, 30.
17 D. Brunel, A. Cauvel, F. Fajula and F. Di Renzo, *Stud. Surf. Sci. Catal.*, 1995, **97**, 173–180.
18 A. Galarneau, D. Desplantier-Giscard, F. Di Renzo and F. Fajula, *Catal. Today*, 2001, **68**, 191–200.
19 D. Brunel, A. C. Blanc, A. Galarneau and F. Fajula, *Catal. Today*, 2002, **73**, 139–152.
20 S. D. Samant, V. P. Raje and R. P. Bhat, *Synlett*, 2006, **16**, 2676–2678.

Downloaded by City College of New York on 22 November 2010
Published on 18 August 2009 on http://pubs.rsc.org | doi:10.1039/B915291C

 This journal is © The Royal Society of Chemistry 2009