

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Postsynthetic modification of mixed-linker metal-organic frameworks for ethylene oligomerization

Cite this: DOI: 10.1039/x0xx00000x

Bing Liu, Suyun Jie,* Zhiyang Bu and Bo-Geng Li

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A series of mixed-linker metal-organic frameworks ($Zn_4O(BDC)_x(ABDC)_{3-x}$) has been synthesized, and then transformed into nickel catalysts for ethylene oligomerization through quantitatively postsynthetic modification. These complexes were more manageable, more stable, and more economic than analogues by post-modification of IRMOF-3 ($x = 0$).

As an emerging class of porous materials, metal-organic frameworks (MOFs) have great prospect in catalysis owing to their high surface area, uniform pore size, controllable structures, and readily tailorable functions.¹⁻⁵ Postsynthetic modification, as an outstanding strategy to overcome the fact that the coordination sphere around the metal ion is completely blocked by the organic linkers, has been developed with MOFs.⁶⁻⁹ In this way, new functional groups or open metal ions which cannot be obtained by direct synthesis will be introduced. However, there is a serious issue being ignored. In some cases, MOFs are not tough enough to suffer from high modification rate,^{10,11} or the density of active centers should not be too high for efficient catalysis, so most of original functional groups are hanging there, which may influence the following catalytic reactions. Up to now, only few work have focused on this problem.¹²⁻¹⁴ Herein, we report the quantitatively postsynthetic modification of a series of mixed-linker MOFs (MixMOFs, $Zn_4O(BDC)_x(ABDC)_{3-x}$) with nickel bromide, and catalyzed oligomerization of ethylene, giving better results than those by direct modification of IRMOF-3.

The synthesis of MixMOFs (MixMOF-a, MixMOF-b, MixMOF-c) was performed by using a similar procedure for IRMOF-3, expect that partial 2-aminobenzene-1,4-dicarboxylate (H_2ABDC) linkers were substituted by 1,4-benzenedicarboxylate (H_2BDC).¹⁵⁻¹⁷ $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in DMF and then the proportional H_2ABDC and H_2BDC were added to the solution. After the mixture was heated at 100 °C for 48 h, the cubic-shape crystals formed were washed with DMF and then soaked in $CHCl_3$. The purity and structural integrity of synthesized MixMOFs were confirmed by powder X-ray diffraction (PXRD), TG and BET analyses. Since the single-crystal data of IRMOF-1 ($x = 0$) and IRMOF-3 ($x = 3$) are very similar,¹⁸ it seems to be obvious that the powder patterns of all the MixMOFs should be more or less identical. Undoubtedly, IRMOF-3 gives the minimum BET surface area because of more

amino groups. To determine the x value in the MixMOFs ($Zn_4O(ABDC)_x(BDC)_{3-x}$), these crystals were digested in DCI/D_2O and $[D_6]DMSO$ and then analyzed by 1H NMR spectroscopy (Fig. 1).^{16,19,20} There is a slightly lower incorporation of amino groups into the MixMOFs than that in the feed (Table 1), which is consistent with the reported results for other mixed-ligand MOFs.^{21,22}

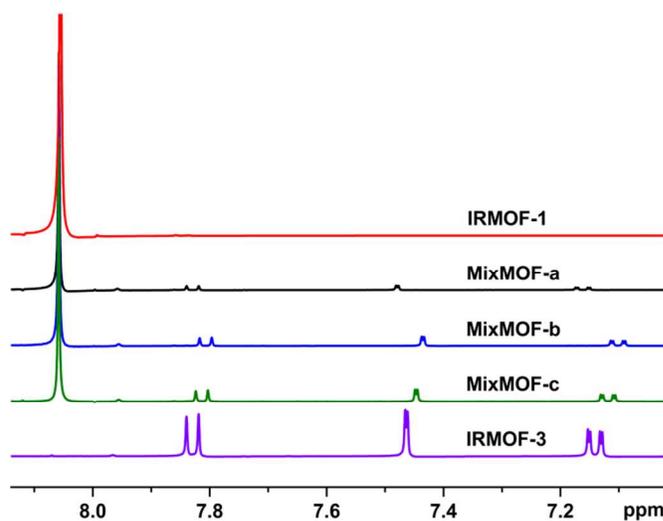
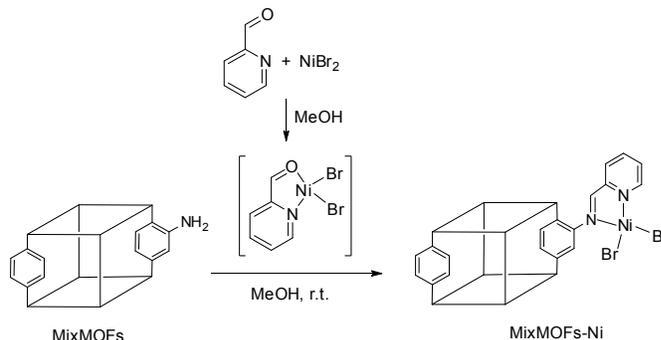


Fig. 1 1H NMR spectra of decomposed samples of IRMOF-1, MixMOFs, and IRMOF-3.

After dried at 100 °C under vacuum for 12 h, all the above MOFs were treated with green solutions containing 2-pyridine carboxaldehyde (PyCHO) and $NiBr_2$ in methanol at room temperature (Table 1).²³ The imine condensation reaction occurred in the presence of excess of $Ni(PyCHO)Br_2$ to directly generate the imino-pyridine nickel complexes anchored into MOFs (Scheme 1). During the reaction, the color of solids slowly changed from light orange to yellowish green for MixMOFs (orange to yellowish green for IRMOF-3). In the FT-IR spectra, apparent amino can be observed for IRMOF-3-Ni, even if the reaction time was prolonged to 4 days (Fig. S1); however, no residual characteristic peaks of amino were found for MixMOFs-Ni after modification (Fig. S2-4),

indicating all the amino groups in MixMOFs have been transformed into imino groups. From this perspective, the reactive groups in MixMOFs can achieve an entire utilization without any waste by using this mixed-linker method.

ICP proved that IRMOF-3 had a limitation of postsynthetic modification and any reinforce in the concentration of starting material and the reaction time would not increase the content of nickel. Whereas, the content of nickel increased along with amino contents in MixMOFs, so the density of active sites could be customized. In other word, the amount of active sites introduced by postsynthetic modification can be controlled by adjusting the ratio of H₂ABDC and H₂BDC during the synthesis of MOFs. As IRMOF-1 exists inevitable ion exchange,²⁴⁻²⁶ the actual measured values are larger than theoretical calculated ones (Table 1).



Scheme 1 The quantitatively postsynthetic modification of MixMOFs to yield MOFs-containing Ni catalysts.

Table 1. Results of synthetic MOFs and their postsynthetic modification

MOFs	Feed ratio of H ₂ ABDC/H ₂ BDC	ABDC/BDC in MixMOFs ^a	NH ₂ content ^a (10 ⁻⁴ mol/g)	Postsynthetic complexes	Time (d)	Ni content (10 ⁻³ mol/g) ^b	Ni content (10 ⁻³ mol/g) ^c
MixMOFs-a	1/5	1.85/10.15	5.95	MixMOFs-a-Ni	1	0.50	0.65
MixMOFs-b	1/3	2.53/9.47	8.12	MixMOFs-b-Ni	2	0.65	1.07
MixMOFs-c	1/2	3.43/8.57	10.95	MixMOFs-c-Ni	3	0.82	1.22
IRMOF-3	1/0	-	36.81	IRMOF-3-Ni-a	1	-	0.17
IRMOF-3	1/0	-	36.81	IRMOF-3-Ni-b	2	-	0.20
IRMOF-3	1/0	-	36.81	IRMOF-3-Ni-c	3	-	0.14
IRMOF-3	1/0	-	36.81	IRMOF-3-Ni-d	4	-	0.18

^a Determined by ¹H NMR. ^b Theoretical value. ^c Measured by ICP.

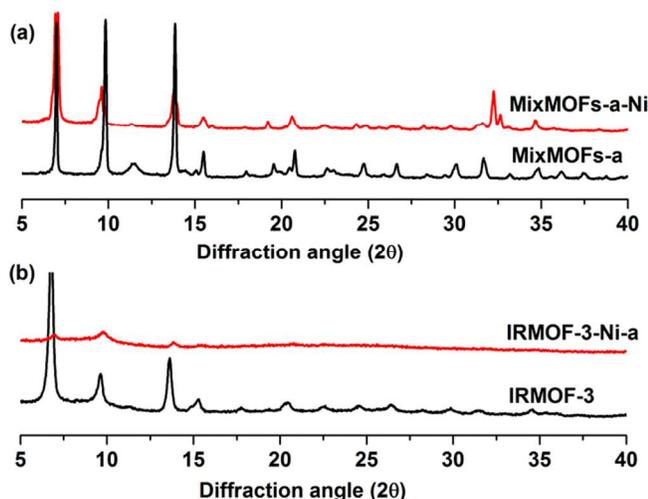


Fig. 2 PXRD patterns of MixMOFs-a and MixMOFs-a-Ni (a), and IRMOF-3 and IRMOF-3-Ni-a (b).

Externally, all the MOFs showed no signs of degradation and maintained their block-like appearance after post-modification. PXRD and N₂ adsorption isotherms methods were carried out to confirm the structural integrity and porosity of the modified MOFs. The nickel catalysts containing MixMOFs retained the structural integrity after modification, showing similar peak positions and intensities (Fig. 2a, S5 and S6). As expected, the post-modification is accompanied by a reasonable decrease of the BET surface (Fig. S10–12 and Table S1). With regard to IRMOF-3, its crystallinity was destroyed very much even with the reaction time of one day and the surface area decayed to single-digit level (Fig. 2b, S7, S11 and Table S1). Therefore, the mix-linker method can also improve the MOFs stability for post-modification. In addition, TGA analysis

indicated that the nickel catalysts containing MixMOFs had better thermal stability than IRMOF-3-Ni (Fig. S8 and S9).

Given the fact that an analogue was very efficient in the selective dimerization of ethylene,²³ the catalytic activity of above nickel catalysts containing MOFs was evaluated in the oligomerization of ethylene in toluene in the presence of Et₂AlCl (Table 2).

Table 2 Results of ethylene oligomerization with MOFs-Ni^a

Entry	Cat.	Activity (10 ⁴ g mol ⁻¹ h ⁻¹)	Selectivity (%) ^b		
			C ₄	C ₆	C ₈₊
1	MOFs ^c	0	0	0	0
2	MOFs+PyCHO ^d	0	0	0	0
3	MOFs+NiBr ₂ ^e	0	0	0	0
4	MixMOFs-Ni-a	5.82	71.3	6.9	21.8
5	MixMOFs-Ni-b	6.91	79.5	7.2	13.2
6	MixMOFs-Ni-c	5.60	79.5	6.2	14.3
7	IRMOF-3-Ni-a	6.29	35.0	9.3	55.7
8	IRMOF-3-Ni-d	5.28	39.6	8.2	52.2
9	MixMOFs-Ni-b ^f	5.41	82.7	2.7	14.6
10	MixMOFs-Ni-b ^g	13.1	92.4	2.6	5.0
11	MixMOFs-Ni-b ^h	46.0	92.7	6.1	1.2
12	MixMOFs-Ni-b ⁱ	18.4	92.3	3.7	4.0

^a Reaction conditions: 30 μmol of Ni, Et₂AlCl: Al/Ni = 100, 150 mL of toluene, 20 bar of ethylene, 20 °C, 30 min. ^b Determined by GC analysis. ^c Including three separate reactions by using 30 mg of IRMOF-1, MixMOFs-b or IRMOF-3. ^d Including three separate reactions by using PyCHO (30 μmol, 3 μL) and 30 mg of IRMOF-1, MixMOFs-b or IRMOF-3. ^e Including three separate reactions by using NiBr₂ (30 μmol, 6.6 mg) and 30 mg of IRMOF-1, MixMOFs-b or IRMOF-3. ^f 10 bar of ethylene. ^g 30 bar of ethylene. ^h 40 °C. ⁱ Al/Ni = 200.

In view of the fact that all three MOFs alone or their mixture with either PyCHO or NiBr₂ didn't show any activity (entries 1-3 in Table 2), it is noteworthy that all the catalysts exhibited comparative activities and gave different selectivity. For IRMOF-3-Ni, its crystallinity has been severely damaged, and the residual amino may affect the reaction process as a Lewis base, giving a worse selectivity for ethylene dimerization (entries 7-8 in Table 2). Instead, the MixMOFs-Ni catalysts retained their structural integrity so that the active Ni centers were thought to be anchored into MOFs,^{27,28} and the corresponding reactions should occur in the hole of MOFs, producing better selectivity for ethylene dimerization. MixMOFs-Ni-a with maximum specific surface area produced more long-chain olefins, and MixMOFs-Ni-b gave the highest activity with appropriate density of active centers. In addition, for this heterogeneous system, reaction conditions would determine the ethylene concentration near the active centers, so that the activity and the selectivity for ethylene dimerization were largely influenced by reaction temperature, ethylene pressure and amount of cocatalyst (entries 5 and 9-12 in Table 2).

Conclusions

In conclusion, a series of mixed-linker metal-organic frameworks (MixMOFs) have been synthesized, which are more stable than IRMOF-3 when they are treated with NiBr₂(PyCHO). The resulting MixMOFs-Ni exhibits higher selectivity for ethylene dimerization than IRMOF-3-Ni. Thus, it is feasible to control the density of metals introduced through postsynthetic modification by adjusting the ratio of linkers containing functional groups during the synthesis of MOFs. This may represent a promising manner to broaden the application of MOFs in industry.

Acknowledgements

The work was supported by the National Basic Research Program of China (No. 2011CB606001) and the Fundamental Research Funds for the Central Universities (No. 2012FZA4025 and 2013FZA4023).

Notes and references

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.

E-mail: jiesy@zju.edu.cn; Tel: (+86)57187951515; Fax: (+86)57187951612.

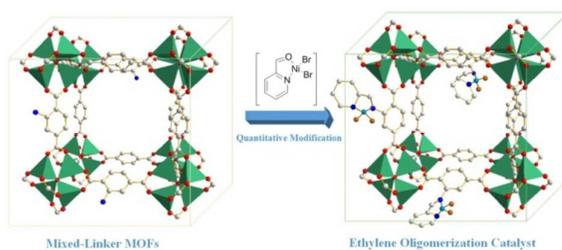
† Electronic Supplementary Information (ESI) available: Experimental procedures, Fig S1–S5 and Table S1. See DOI: 10.1039/c000000x/

- M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, O. K. Farha and J. T. Hupp, *Angew. Chem. Int. Ed.* 2014, **53**, 497–501.
- O. Kozachuk, I. Luz, F. X. Llabrés I Xamena, H. Noei, M. Kauer, H. B. Albada, E. D. Bloch, B. Marler, Y. Wang, M. Muhler and R. A. Fischer, *Angew. Chem. Int. Ed.* 2014, **53**, 7058–7062.
- V. N. Panchenko, M. M. Matrosova, J. Jeon, J. W. Jun, M. N. Timofeeva and S. H. Jung, *J. Catal.* 2014, **316**, 251–259.
- Y. Chen, X. Huang, X. Feng, J. Li, Y. Huang, J. Zhao, Y. Guo, X. Dong, R. Han, P. Qi, Y. Han, H. Li, C. Hu and B. Wang, *Chem. Commun.* 2014, 8374–8377.
- R. Lin, L. Shen, Z. Ren, W. Wu, Y. Tan, H. Fu, J. Zhang and L. Wu, *Chem. Commun.* 2014, 8533–8535.
- S. M. Cohen, *Chem. Rev.* 2012, **112**, 970–1000.
- Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.* 2007, **129**, 12368–12369.
- Z. Wang and S. M. Cohen, *Chem. Soc. Rev.* 2009, **38**, 1315–1329.
- K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.* 2011, **40**, 498–519.
- M. J. Ingleson, J. Perez Barrio, J. Guilbaud, Y. Z. Khimiyak and M. J. Rosseinsky, *Chem. Commun.* 2008, 2680–2682.
- K. K. Tanabe, Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.* 2008, **130**, 8508–8517.
- A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, *Angew. Chem. Int. Ed.* 2008, **47**, 8482–8486.
- Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.* 2009, **48**, 296–306.
- C. A. Allen and S. M. Cohen, *J. Mater. Chem.* 2012, **22**, 10188–10194.
- J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.* 2006, **128**, 1304–1315.
- K. Koh, A. G. Wong-Foy and A. J. Matzger, *Chem. Commun.* 2009, 6162–6164.
- W. Kleist, F. Jutz, M. Maciejewski and A. Baiker, *Eur. J. Inorg. Chem.* 2009, 3552–3561.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science* 2002, **295**, 469–472.
- Z. Wang and S. M. Cohen, *Angew. Chem. Int. Ed.* 2008, **47**, 4699–4702.
- E. Dugan, Z. Wang, M. Okamura, A. Medina and S. M. Cohen, *Chem. Commun.* 2008, 3366–3368.
- H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science* 2010, **327**, 846–850.
- A. D. Burrows, L. C. Fisher, C. Richardson and S. P. Rigby, *Chem. Commun.* 2011, **47**, 3380–3382.
- J. Canivet, S. Aguado, Y. Schuurman and D. Farrusseng, *J. Am. Chem. Soc.* 2013, **135**, 4195–4198.
- C. K. Brozek and M. Dincă, *Chem. Sci.* 2012, **3**, 2110–2113.
- C. K. Brozek and M. Dincă, *J. Am. Chem. Soc.* 2013, **135**, 12886–12891.
- C. K. Brozek, L. Bellarosa, T. Soejima, T. V. Clark, N. López, M. Dincă, *Chem. Eur. J.* 2014, **20**, 6871–6874.
- X. Zhang, F. X. Llabrés I Xamena, A. Corma, *J. Catal.* 2009, **265**, 155–160.
- B. Liu, S. Jie, Z. Bu and B.-G. Li, *J. Mol. Catal. A: Chem.* 2014, **387**, 63–68.

A table of contents entry
for

Postsynthetic modification of mixed-linker metal-organic frameworks for ethylene oligomerization

Bing Liu, Suyun Jie,* Zhiyang Bu and Bo-Geng Li



MOFs-containing nickel catalysts have been synthesized through postsynthetic modification of mixed-linker MOFs ($\text{Zn}_4\text{O}(\text{BDC})_x(\text{ABDC})_{3-x}$) and used for ethylene oligomerization.