RSC Advances

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Toyao, M. Fujiwaki, Y. Horiuchi and M. MATSUOKA, *RSC Adv.*, 2013, DOI: 10.1039/C3RA44701D.

RSC Advances



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/advances Registered Charity Number 207890

ARTICLE TYPE

Application of an amino-functionalised metal-organic framework: An approach to a one-pot acid-base reaction

Takashi Toyao, Mika Fujiwaki, Yu Horiuchi* and Masaya Matsuoka*

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

The amino-functionalised metal-organic framework, MIL-101(Al)-NH₂, has been synthesized by using a solvothermal method and employed as a bifunctional acid-base catalyst for a one-pot, sequential deacetalization-Knoevenagel condensation reaction. In preliminary studies, the abilities of MIL-101(Al)-NH₂ to serve as an acid and base catalyst were explored separately by two typical acid- and base-

¹⁰ catalysed reaction, that is, deacetalization of benzaldehyde dimethylacetal and Knoevenagel condensation of benzaldehyde with malononitrile. MIL-101(Al)-NH₂ was found to catalyse each of these reactions with a high efficiency. MIL-101(Al)-NH₂ was then employed as a catalyst for the one-pot sequential deacetalization-Knoevenagel condensation reaction between benzaldehyde dimethylacetal and malononitrile. Benzylidenemalononitrile as the final product was successfully generated with a high yield

¹⁵ via benzaldehyde over MIL-101(Al)-NH₂. In addition, the catalytic ability of MIL-101(Al)-NH₂ was demonstrated to be superior to those of conventional heterogeneous, homogeneous as well as other functionalised metal-organic framework catalysts. Finally, the results show that MIL-101(Al)-NH₂ can be reused as a catalyst for this process without significant loss of its activity.

20 Introduction

Recently, synthetic organic chemists have given great attention to the development of one-pot, sequential organic reactions owing to their comparably higher efficiencies, increased cost effectiveness and reduced formation of waste materials.¹ An ²⁵ important goal in this area, is the development of new catalysts having spatially isolated, multiple active sites so that they can

- promote multi-step reaction cascades. Among the various systems designed to possess this capability, many of these are homogeneous catalysts and, as a result, they generally suffer from ³⁰ product contamination and limited recyclability.² Furthermore,
- ³⁵ product containingtion and mined tecyclability. Furthermore, catalytic acid-base one-pot reaction systems are hardly developed in the homogeneous phase because the acid and base sites are easily deactivated by each other. Therefore, the development of multifunctional heterogeneous catalysts that promote one-pot ³⁵ reactions is currently receiving much attention.³
- Metal-organic frameworks (MOFs), also called porous coordination polymers (PCPs), have gained recent interest because of their several attractive properties, including high specific surface areas, well-ordered porous structures and
- ⁴⁰ structural designability.⁴ Because of these advantageous features,

MOFs have been widely investigated as solid catalysts or catalyst supports for several organic transformations, such as epoxidations,⁵ cycloadditions of CO₂ with epoxides,⁶ aldol condensations,⁷ Knoevenagel condensations⁸ and Paal-Knorr ⁴⁵ reactions.⁹ In addition, because their topology and surface functionalities can be readily tuned by modifying or varying the core metal-oxo clusters and bridging organic linkers, MOFs have emerged as interesting platforms for engineering molecular solids to create multifunctional catalysts. Several multifunctional MOF ⁵⁰ based catalytic systems have been devised¹⁰ so that reactions are promoted by functionality in organic linkers or by coordinatively unsaturated metal sites of MOFs. Moreover, catalytic sites in these substances can be incorporated by using postsynthetic modification of organic struts.

⁵⁵ The coordinatively unsaturated metal sites within MOFs, which can serve as catalytic centres, have been actively investigated in recent years.¹¹ These studies have shown that the sites are capable of acting as Lewis acid catalysts for various organic reactions. Because structural defects are thought to be ⁶⁰ responsible for catalysis by these MOFs, efforts have been made to enhance activities by deliberately introducing defects.¹² Although many reports exist describing the Lewis acidity of MOFs, the Brønsted acidity of these substances has not been studied greatly. However, very recently, Ameloot et al. reported ⁶⁵ that Brønsted acid sites are present in MOFs and that they are responsible for catalysis of the oligomerization of furfuryl alcohol.¹³ The Brønsted acidities of MOFs are attributed to the

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

E-mail:horiuchi@chem.osakafu-u.ac.jp; matsumac@chem.osakafu-u.ac.jp; Fax: +81-72-254-9910; Tel: +81-72-254-9288

presence of carboxylic acid moieties (-COOH groups) in the organic linker existing on the outer surface of the particles and in structural defects within the framework. Consequently, new reactions and multi-step processes that can be catalysed by 5 Brønsted acid sites present in MOFs would have great utility in organic synthesis.

In the study described below, we examined the acid and base properties of the amino-functionalised MOF, MIL-101(Al)-NH₂, in the context of catalysis of deacetalization and Knoevenagel 10 condensation reactions. It is well-known that deacetalization reactions are catalysed by Brønsted acidic sites¹⁴ and Knoevenagel condensation reactions are catalysed by Brønsted and Lewis base sites.¹⁵ The results show that the respective reactions are successfully promoted by MIL-101(Al)-NH₂. The 15 possibility that the amino-functionalised MOF can serve as a bifunctional acid-base catalyst has been demonstrated using a one-pot reaction producing benzylidenemalononitrile via sequential deacetalization and Knoevenagel condensation (Scheme 1). Finally, observations made in this effort show that 20 activity of MIL-101(Al)-NH2 as acid-base bifunctional catalysts is superior to those of conventional heterogeneous, homogeneous as well as other MOF catalysts.



30 Scheme 1. One-pot deacetalization-Knoevenagel condensation reaction.

Experimental

Materials

Published on 09 September 2013. Downloaded by Clemson University on 16/09/2013 07:46:15.

2-Amino-benzenedicarboxylic acid (H₂BDC-NH₂), 1,4³⁵ benzenedicarboxylic acid (H₂BDC), N'N-dimethylformamide (DMF), ZrCl₄, Cr(NO₃)₃·9H₂O, NaOH, HCl, methanol, acetone, triethylamine and 1, 4-dioxane were purchased from Nacalai Tesque Inc. 1,3,5-Benzenetricarboxylic acid (H₂BTC), malononitrile, benzaldehyde and benzaldehyde dimethylacetal
⁴⁰ were purchased from Tokyo Chemical Industry Co., Ltd. AlCl₃·6H₂O, Al(NO₃)₃·9H₂O, Cu(NO₃)₃·3H₂O and MgO were purchased from Kishida Chemical Co., Ltd. Al₂O₃ was purchased from ZEOLYST. All materials were used as received without
⁴⁵ purification.

Catalysts preparation

MIL-101(Al)-NH₂ was synthesized using the previously-reported method.¹⁶ The mixture of AlCl₃·6H₂O (0.51 g), H₂BDC-NH₂ (0.56 g) and DMF (40 ml) was subjected to solvothermal reaction

⁵⁰ conditions in a Teflon-lined stainless steel autoclave for 40 h at 403 K under autogenous pressure. The generated precipitate was separated by filtration, washed repeatedly with acetone and dried under vacuum for 3 h at room temperature.

General methods

⁵⁵ Standard θ -2 θ X-ray diffraction (XRD) data were recorded on a Shimadzu X-ray diffractmeter XRD-6100 using Cu K α radiation ($\lambda = 1.5406$ Å). Nitrogen adsorption-desorption isotherms were collected by using a BEL-SORP mini (BEL Japan, Inc.) at 77 K. FT-IR spectra were recorded in transmittance mode by a FT-IR

⁶⁰ spectrophotometer equipped with a DTGS detector (JASCO FT/IR 660Plus, resolution 4 cm⁻¹). Self-supporting pellets of the samples were loaded in a specially constructed IR cell, which was equipped with CaF_2 windows. Thermogravimetric (TG) analysis was carried out using a thermal analyser (Rigaku Termoplus

⁶⁵ 8120), with a heating rate of 10 K min⁻¹ in air. Scanning electron microscope (SEM) images were obtained with a Hitachi S-4500.

Catalytic reactions

Deacetalization reaction: The reactions were carried out in liquid phase in a 35 ml glass reactor. A solution of benzaldehyde ⁷⁰ dimethylacetal (1 mmol) and 1, 4-dioxane (4 ml) was stirred at 363 K with 100 mg of the catalysts in powder form. The progression of the reaction was monitored by using gas chromatography (Shimadzu GC-14B with a flame ionization detector) equipped with an InertCap [®]1 capillary column.

Knoevenagel condensation reaction: The reactions were carried out in liquid phase in a 35 ml glass reactor. A solution of benzaldehyde (1 mmol), malononitrile (5 mmol) and 1, 4-dioxane (4 ml) was stirred at 363 K with 100 mg of the catalysts in ⁸⁰ powder form. The progression of the reaction was monitored by using gas chromatography (see above).

One-pot deacetalization-Knoevenagel condensation reaction: The reactions were carried out in liquid phase in a 35 ml glass

- 85 reactor. A solution of benzaldehyde dimethylacetal (1 mmol), malononitrile (5 mmol) and 1, 4-dioxane (4 ml) were stirred at 363 K with 100 mg of the catalysts in powder form. The progression of the reaction was monitored by using gas chromatography (see above).
- Reusability of the catalyst was studied as follows. After the first run, the catalyst was washed three times with 1, 4-dioxane, dried at 313 K in air and reused for the next run. The above procedure was repeated three times.

Results and discussion

95 The amino-functionalised MOF catalyst, MIL-101(Al)-NH₂, was prepared from AlCl₃·6H₂O and H₂BDC-NH₂ by using the previously described solvothermal method.¹⁶ XRD and N₂ adsorption-desorption measurements were performed to confirm the formation of the MOF structure. Figure 1 shows an XRD 100 pattern of MIL-101(Al)-NH₂. Although the diffraction pattern does not perfectly match the diffraction pattern previously reported, the pattern can be attributable to a MIL-101 type structure.¹⁷ In addition, because no diffraction patterns corresponding to the bulk Al₂O₃ are observed, it is confirmed that 105 crystalline Al₂O₃ are not formed in MIL-101(Al)-NH₂. Figure 2 represents N₂ adsorption-desorption isotherm of MIL-101(Al)-NH₂. This isotherm shows the well-known characteristic steps of the MIL-101 type structure. The changes present in isotherm correspond to filling only the superoctahedra at low relative ¹¹⁰ pressures ($P/P_0 < 0.05$) and, as the pressure increases, medium Published on 09 September 2013. Downloaded by Clemson University on 16/09/2013 07:46:15.



30 Fig. 2. N₂ adsorption-desorption isotherm of MIL-101(Al)-NH₂.

 $(P/P_0 = 0.15)$ and large cavities of the MOF become filled. By using the BET (Brunauer-Emmett-Teller) method to treat the N₂ adsorption data, the specific surface area of MIL-101(Al)-NH₂ ³⁵ was calculated to be 800 m²g⁻¹. This value is lower than the one previously reported,¹⁶ indicating that some structural defects exist in the sample of MIL-101(Al)-NH₂ prepared in this study. Despite leading to a low specific surface area of this material, the structural defects can be key features required to develop ⁴⁰ catalysts which exhibit better performances, as suggested by Corma et al.¹⁸

In order to further confirm the structural features, FT-IR and TG analyses were performed (see Figs. S1 and S2 in the Supporting Information). The FT-IR spectrum of MIL-101(Al)-⁴⁵ NH₂ shows bands corresponding to the symmetric and asymmetric stretching of primary amines (3408 and 3521 cm⁻¹), indicating that the –NH₂ groups are free without coordination. As shown in Fig. S2, MIL-101(Al)-NH₂ releases water followed by desorption of some DMF and decomposes at temperatures above ⁵⁰ 650 K. This result indicates high thermal stability of MIL-

101(Al)-NH₂ prepared in this study.

Prior to exploring applications to one-pot reactions, separate deacetalization of benzaldehyde dimethylacetal and Knoevenagel condensation of benzaldehyde with malononitrile were performed

⁵⁵ over MIL-101(Al)-NH₂ as test reactions. Both reactions are widely used in organic chemistry.¹⁹ In general, deacetalization reactions are well-known to be catalysed over Brønsted acidic sites.¹⁴ On the other hand, Knoevenagel condensation reactions are catalysed over Brønsted and Lewis base sites.¹⁵ Therefore, ⁶⁰ this study was conducted to investigate the activities of the respective Brønsted acid and base sites in MIL-101(Al)-NH₂. For comparison purposes, the activities of MIL-101(Al)-NH₂ in these reactions were compared to those of HY zeolite (SiO₂/Al₂O₃ = 30) and MgO, which are conventional acid and base catalysts, ⁶⁵ respectively. As shown in Fig. 3, inspection of the time courses for the production of benzaldehyde in deacetalization reactions of benzaldehyde dimethylacetal shows that MIL-101(Al)-NH₂ and HY zeolite serve as efficient catalysts for this process while benzaldehyde is not generated when MgO is used. The results ⁷⁰ suggest that carboxylic acid groups (–COOH) present on outer surfaces or at defect sites in MIL-101(Al)-NH₂ act as effective Brønsted acids.

Subsequently, Knoevenagel condensation reactions of benzaldehyde with malononitrile were carried out using MIL-⁷⁵ 101(Al)-NH₂, HY zeolite and MgO. The time courses displayed in Fig. 4 demonstrate that MIL-101(Al)-NH₂ is an effective catalyst of this reaction, whereas MgO has a lower activity and the reaction does not proceed when HY zeolite is employed. These findings suggest that the -NH₂ groups in MIL-101(Al)-⁸⁰ NH₂ act as base sites to promote the Knoevenagel condensation

reaction. Furthermore, it is noteworthy that the reaction rate for MIL-101(Al)-NH₂ is much higher than that for MgO. This result



Fig. 3. Time course of the deacetalization reaction over MIL-101(Al)-NH₂ (\bullet), HY zeolite (\blacksquare) and MgO (\bullet).



Fig. 4. Time course of the Knoevenagel condensation reaction over MIL-115 101(Al)-NH₂ (\bullet), HY zeolite (\blacksquare) and MgO (\bullet).

is attributable to the presence of -NH₂ groups in MIL-101(Al)-NH₂. It is well-known that the Knoevenagel condensation reaction undergoes through the formation of imine intermediate on the catalysts containing organic amines, followed by the ⁵ addition of active methylene group.²⁰ Therefore, it can be considered that the reaction is promoted more efficiently over MIL-101(Al)-NH₂ with -NH₂ groups than over MgO. As explored above, the results emanating from the above effort show that MIL-101(Al)-NH₂ possesses both Brønsted acid and base ¹⁰ sites that serve as catalysts for respective deacetalization and Knoevenagel condensation reactions.

The potential use of MIL-101(Al)-NH₂ as a bifunctional acidbase catalyst for one-pot reactions was investigated next. For this purpose, MIL-101(Al)-NH₂ was employed to promote the 15 benzylidenemalononitrile (3a) forming reaction between benzaldehyde dimethylacetal and malononitrile that takes place through sequential deacetalization and Knoevenagel condensation processes. Inspection of the time course of the process displayed in Fig. 5 shows that benzylidenemalononitrile is efficiently 20 generated from benzaldehyde dimethylacetal (1a) via a pathway involving initial formation of benzaldehyde (2a), and that the vield of 3a reaches 94% after a 3 h reaction time. It is also shown that the reaction does not take place in the absence of a catalyst (entry 17 in Table 1). These observations clearly demonstrate that 25 MIL-101(Al)-NH₂ serves as an effective bifunctional acid-base catalyst for the sequential deacetalization and Knoevenagel condensation reaction.



Fig. 5. Time course of the one-pot deacetalization-Knoevenagel condensation reaction over MIL-101(Al)-NH₂; benzaldehyde dimethylacetal (\blacklozenge), benzaldehyde (\blacksquare), benzylidenemalononitrile (\blacklozenge).

For comparison purposes, conventional solid and homogeneous as well as other MOF catalysts were applied for this one-pot acid-base reaction with the results summarized in Table 1. When HY zeolite is used as the catalyst (entry 2), the ⁵⁰ second step, involving Knoevenagel condensation of benzaldehyde with malononitrile, does not take place efficiently. As a result, only benzaldehyde is produced because HY zeolite only serves as an acid catalyst for the deacetalization step. In addition, when MgO is employed (entry 3), the reaction between ⁵⁵ the acetal and malononitrile does not occur because the first step

in the pathway does not take place. These results clearly demonstrate that the existence of both acid and base sites, like those found in MIL-101(Al)-NH₂, are necessary for promotion of

the one-pot benzylidenemalononitrile forming process. ⁶⁰ Observation made in additional studies show that Al₂O₃ does not promote this reaction, suggesting that possible impurities in MIL-101(Al)-NH₂ comprised of aluminum oxide are not responsible for the observed catalytic activity (entry 4). Also, the one-pot reaction takes place when a mixture of HY zeolite and MgO is ⁶⁵ utilized (entry 5), but the reaction rate is much lower than that of the MIL-101(Al)-NH₂ catalysed process. These facts suggest that MIL-101(Al)-NH₂ behaves as an efficient bifunctional acid-base catalyst compared to conventional solid catalysts.

In addition, homogeneous catalysts such as HCl and ⁷⁰ triethylamine were used for the one-pot reaction. The presence of the acid catalyst (HCl) leads to quantitative deprotonation of dimethylacetal to benzaldehyde but does not lead to the formation of **3a** (entry 6). On the other hand, the starting substrate remains unchanged when using triethylamine as a catalyst even after 3 h ⁷⁵ (entry 7). Furthermore, the reaction hardly occurs even the first step of the reaction when the mixture of HCl and triethylamine is employed as the catalyst (entry 8). In the homogeneous systems, acid and base catalysts are easily neutralised, resulting in the deactivation of the catalysts.

⁸⁰ Various MOF catalysts such as MIL-53(Al)-NH₂, MIL-53(Al), MIL-101(Cr)-NH₂, MIL-101(Cr), Zr-MOF-NH₂, Zr-MOF, Cu-MOF and Ca-MOF²¹ were also employed for the one-pot reaction (entry 9–16).²² Among the catalysts explored in this study, MIL-101(Al)-NH₂ was found to exhibit the highest catalytic activity ⁸⁵

 Table 1. One-pot deacetalization-Knoevenagel condensation

 reaction using various catalysts^a.



Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	3a
1	MIL-101(Al)-NH ₂	100	6	94
2	HY zeolite	88	79	9
3	MgO	7	6	1
4	Al_2O_3	14	1	3
5	HY zeolite + MgO ^b	67	39	20
6	HCl ^c	100	95	5
7	Triethylamine ^c	3	1	2
8	HCl + Triethylamine ^d	15	5	8
9	MIL-53(Al)-NH ₂	100	81	18
10	MIL-53(Al)	14	9	5
11	MIL-101(Cr)-NH ₂	86	2	84
12	MIL-101(Cr)	60	19	38
13	Zr-MOF-NH ₂	99	75	23
14	Zr-MOF	85	57	26
15	Cu-MOF	79	69	7
16	Ca-MOF	38	34	2
17	No catalyst	2	0	2

^a Reaction conditions: Benzaldehyde dimethylacetal (1 mmol),
 ⁹⁵ malononitrile (5 mmol), 1, 4-dioxane (4 mL), catalyst (100 mg), 363 K, 3
 ^b The mixture of HY zeolite (50 mg) and MgO (50 mg) was employed as the catalyst. ^c 0.1 mmol of the catalyst was used. ^d The mixture of HCI (0.1 mmol) and triethylamine (0.1 mmol) was employed as the catalyst.

RSC Advances Accepted Manuscript

Published on 09 September 2013. Downloaded by Clemson University on 16/09/2013 07:46:15.

for the one-pot reaction. This result is attributable to the presence of $-NH_2$ groups and its large pore size (window size = $1.2 \times$ 1.6Å).¹⁶ Specifically, the -NH₂ groups promote the second condensation step of the reaction, and the large pore sizes enable 5 facile diffusion of the substrates and products. Although MIL-101(Cr)-NH₂ has both -NH₂ groups and the same pore size as MIL-101(Al)-NH₂, its catalytic activity is lower than that of MIL-101(Al)-NH₂ (entry 11). To clarify the origin of the difference in the activity, SEM observations were conducted, as displayed in 10 Fig. S3. The large particle size ranging from 200 nm to 400 nm is observed for MIL-101(Al)-NH₂ compared to the particle size of MIL-101(Cr)-NH₂ (50–100 nm). Since the Brønsted acidities are attributed to -COOH groups in the organic linker existing on the outer surface of the particles and in structural defects within the 15 framework, the small particles are expected to be favorable for the reaction. On the other hand, however, these SEM images also reveal that MIL-101(Al)-NH₂ has lower crystallinity than MIL-101(Cr)-NH₂, suggesting that larger amounts of structural defects exist in MIL-101(Al)-NH₂. Therefore, the results of the one-pot 20 reaction can be rationalized by the amount of structural defects. As a consequence, MIL-101(Al)-NH₂ exhibits better performance in the one-pot reaction. Interestingly, MOF catalysts possessing -NH₂ groups not only promote the Knoevenagel condensation reaction but also catalyse the first deacetalization step more 25 efficiently than those without primary amine moieties (entry 9, 11, 13). This outcome is associated with the cooperative effect of acid and base groups that lead to acceleration of the aldehyde forming process. In addition, it should be noted that the condensation step of the reaction is catalysed by some MOF 30 catalysts that do not contain -NH2 groups (entry 12, 14). In general, Knoevenagel condensation reactions are promoted by not only base catalysts but also Lewis acid catalysts.²³ As mentioned

- in the introduction, it has been widely studied that coordinatively unsaturated metal sites of MOFs can act as Lewis acid catalysts. ³⁵ These facts suggest that coordinatively unsaturated metal sites of
- MOFs catalyse the second step of the reaction, resulting in the



Fig. 6. Recycling tests for the one-pot deacetalization-Knoevenagel condensation reaction over MIL-101(Al)-NH₂. Reaction conditions: Benzaldehyde dimethylacetal (1 mmol), malononitrile (5 mmol), 1, 4-dioxane (4 mL), catalyst (100 mg), 363 K, 3 h.

ss formation of **3a** as the final product. From these comparison studies, it was revealed that the activity of MIL-101(Al)-NH₂ as an acid-base bifunctional catalyst is superior to those of conventional heterogeneous, homogeneous as well as other MOF

catalysts.

⁶⁰ Finally, recycling experiments were carried out for the evaluation of the reusability of MIL-101(Al)-NH₂. The catalyst after the reaction for 3 h was washed with 1, 4-dioxane, dried at 313 K and then reused for the next run. As shown in Fig. 6, MIL-101(Al)-NH₂ can be reused at least three times with the retention ⁶⁵ of high catalytic activity and selectivity.

Conclusions

The results of the investigation described above show that the amino-functionalised MOF, MIL-101(Al)-NH₂, serves as a 70 bifunctional acid-base catalyst. The initial studies reveal that MIL-101(Al)-NH₂ promotes both the deacetalization of benzaldehyde dimethylacetal and Knoevenagel condensation of benzaldehyde with malononitrile. Moreover, owing to the presence of Brønsted acid and base sites, MIL-101(Al)-NH₂ 75 promotes the one-pot reaction of benzaldehyde dimethylacetal and malononitrile to produce benzylidenemalononitrile. In addition, the results show that MIL-101(Al)-NH₂ exhibits higher catalytic activities than conventional heterogeneous acid and base as well as various MOF catalysts for the one-pot acid-base 80 reaction. Lastly, MIL-101(Al)-NH₂ can be recycled at least three times without significant loss of its catalytic activity. The observations made in this effort suggest new possibilities to design catalysts for one-pot reactions utilizing MOF materials.

Ackowledgements

⁸⁵ The present work is supported by a Grant-in-Aid for Scientific Research (KAKENHI) from Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 21550192). The authors thank Prof. M. Tatsumisago, Dr. A. Hayashi and Mr. T. Matsuyama for TG analysis. T. T. thanks the JSPS Research ⁹⁰ Fellowships for Young Scientists.

Notes and references

- (a) J. M. Lee, Y. Na, H. Han and S. Chang, *Chem. Soc. Rev.*, 2004, 33, 302; (b) H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.* 1994, 94, 2483; (c) L.C. Wasilke, S. L. Obrey, R. T.
- *Chem. Rev.*, 1994, **94**, 2483; (c) J. C. Wasilke, S. J. Obrey, R. T. Baker and G. C. Bazan, *Chem. Rev.*, 2005, **105**, 1001.
- 2 (a) C. Gunanathan, Y. Ben-David and D. Milstein, *Science*, 2007, 317, 790; (b) V. Cadierno, J. Francos, J. Gimeno and N. Nebra, *Chem. Commun.*, 2007, 24, 2536; (c) T. Zweifel, J.-V. Naubron and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 2009, 48, 559.
- 3 (a) K. Motokura, M. Tada and Y. Iwasawa, J. Am. Chem. Soc., 2009, 131, 7944; (b) S. Shylesh, A. Wagener, A. Seifert, S. Ernst and W. R. Tiel, Angew. Chem., Int. Ed., 2010, 49, 184; (c) A. Corma, T. Rodenas and M. J. Sabater, Chem. Eur. J. 2010, 16, 254; (d) Y.
- ¹⁰⁵ Huang, S. Xu, and V. S. Y. Lin, *Angew. Chem., Int. Ed.*, 2011, **50**, 661; (e) N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown and G. Rothenberg, *Angew. Chem., Int. Ed.*, 2011, **50**, 9615; (f) M. Sasidharan, S. Fujita, M. Ohashi, Y. Goto, K. Nakashima and S. Inagaki, *Chem. Commun.*, 2011, **47**, 10422; (g) A. Corma, T. Rodenas and M. J. Sabater, *J. Catal.* 2011, **279**, 319; (i) Y. Shiraishi, K. Fujiwara, Y. Sugano, S. Ichikawa and T. Hirai, *ACS catalysis*, 2013, **3**, 312.
- 4 (a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (b) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (c) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; (d) X. Zhao, B. Xiao, A. J.

Fletcher, K. Thomas, D. Bradshaw and M. J. Rosseinsky, Science, 2004, 306, 1012; (e) S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, Nature Chem., 2010, 2, 633; (f) A. Corma, H. Garcia and F.

- X. Liabres i Xamena, Chem. Rev., 2010, 110, 4606; (g) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, Chem. Soc. Rev., 2009, 38, 1450.
- (a) F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, J. Am. 5 Chem. Soc., 2010, 132, 15390; (b) M. Saito, T. Toyao, K. Ueda, T. Kamegawa, Y. Horiuchi and M. Matsuoka, Dalton Trans., 2013, 42, 10 9444.
- J. Song, Z. Zhang, S. Hu, T. Xu, T. Jiang and B. Han, Green Chem., 6 2009. 11. 1031.
- 7 F. Vermoortele, R. Ameloot, A. Vimont, C. Serre and D. D. Vos, 15 Chem. Commum., 2011, 47, 1521.
- J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink 8 and F. Kapteijn, J. Catal., 2009, 261, 75.
- 9 N. T. S. Phan, T. T. Nguyen, Q. H. Luu and L. T. L. Nguyen, J. Mol. Catal. A: Chem., 2012, 362, 178
- 20 10 (a) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi and S. Feng, Chem. Commun., 2012, 48, 6151; (b) R. Srirambalaji, S. Hong, R. Natarajan, M. Yoon, R. Hota, Y. Kim, Y. H. Ko and K. Kim, Chem. Commun., 2012, 48, 11650; (c) J. Park, J. R. Li, Y. P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L. B. Sun, P. B. Balbuena and H. C. 25
- Zhou, Chem. Commun., 2012, 48, 9995; (d) F. G. Cirujano, F. X. Llabrés i Xamena and A. Corma, Dalton Trans., 2012, 41, 4249; (e) F. Vermoortele, R. Ameloot, A. Vimont, C. Serre and D. D. Vos, Chem. Commun., 2011, 47, 1521.
- 11 (a) M. Opanasenko, A. Dhakshinamoorthy, M. Shamzhy, P. Nachtigall, M. Horáček, H. Garcia and J. Čejka, Catal. Sci. Technol., 2013, 3, 500; (b) L. Mitchell, B. G. Santiago, J. P.S. Mowat, M. E. Gunn, P. Williamson, N. Acerbi, M. L. Clarke and P. A. Wright, Catal. Sci. Technol., 2013, 3, 606.
- 12 U. Ravon, M. Savonnet, S. Aguado, M. E. Domine, E. Janneau and D. Farrusseng, Micropor. Mesopor. Mater., 2010, 129, 319.
- R. Ameloot, F. Vermoortele, J. Hofkens, F. C. D. Schryver, D. E. D. 13 Vos and M. B. J. Roeffraers, Angew. Chem., Int. Ed., 2013, 52, 401.
- 14 (a) R. A. Duval, R. L. Allmon and L. R. Lever, J. Med. Chem., 2007, 50, 2144; (b) F. Douelle, A. S. Capes and M. F. Greaney, Org. Lett., 2007. 9. 931
- 15 S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, J. Am. Chem. Soc., 2007, 129, 2607.
- 16 P. S. Crespo, E. V. R. Fernandez, J. Gascon and F. Kapteijin, Chem. Mater., 2011, 23, 2565.
- 45 17 D. Y. Hong, Y. K. Hwang, C. Serre, G. Ferey and J. S. Chang, Adv. Funct. Mater., 2009, 19, 1537.
- 18 F. X. Liabres i Xamena, F. G. Cirujano and A. Corma, Micropor. Mesopor. Mater., 2012, 157, 112.
- (a) W. Li, J. Li, Y. Wu, N. Fuller and M. A. Markus, J. Org. Chem., 19 2010, 75, 1077; (b) Y. Zhang, Q. Dou, L. Dai, X. Wang and Y. Chen, RSC Adv., 2012, 2, 8979; (c) F. Bigi, M. L. R. Maggi, A. Piccinno, G. Sartori, Green Chem., 2000, 2, 101; (d) Y.-Q. Yu, Z.-L. Wang, J. Chin. Chem. Soc., 2013, 60, 288.
- 20 M. Hartmann and M. Fischer, Micropor. Mesopor. Mater., 2012, 164, 55 38.
- Various MOF catalysts were synthesized by the recently reported 21 methods; see ref. 16 for MIL-53(Al)-NH2 and MIL-53(Al), Y. Lin, C. Kong and L. Chen, RSC Adv., 2012, 2, 6417 for MIL-101(Cr)-NH₂ and MIL-101(Cr), J. H. Cavka, S. Jakobsen, U. Olsbye, N.
- Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, J. Am. Chem. Soc., 2008, 130, 13850 for Zr-MOF-NH2 and Zr-MOF, S. Loera-Serna, M. A. Oliver-Tolentino, M. D. Lopez-Nunez, A. Santana-Cruz, A. Guzman-Vargas, R. Cabrera-Sierra, H. I. Beltran and J. Flores, J. Alloys Compd., 2012, 540, 113 for Cu-MOF and M. Mazaj, G. Mali, M. Rangus, E. Zunkovic, V. Kaucic and N. Z. Logar, J. 65
- Phys. Chem. C, 2013, 117, 7552 for Ca-MOF.
- 22 In this study, many attempts have been done to synthesize MIL-101(Al) without -NH2 groups. However, all attempts failed to make MIL-101(Al) as is the case with the previous report; see ref. 16.
- 70 23 M. J. Climent, A. Corma, S. Iborra and A. Velty, J. Mol. Catal. A: Chem., 2002, 327, 182.



RSC Advances Accepted Manuscript