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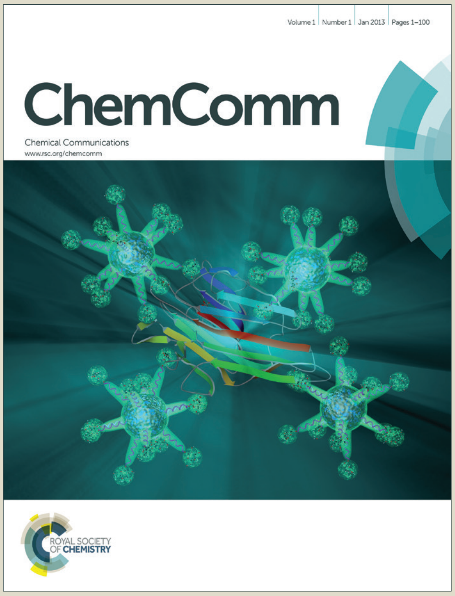

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## COMMUNICATION

# One-pot synthesis of Pd@MOF composites without the addition of stabilizing agents

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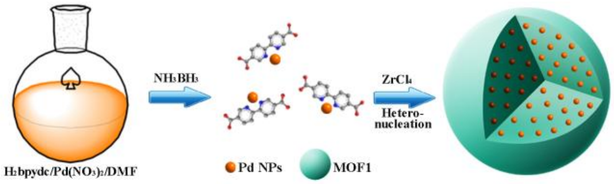
**In this work, the first example of a facile one-pot route for the synthesis of Pd@MOF composite without additional stabilizing agents is developed. The as-synthesized MOF composite shows high activity and chemoselectivity in the hydrogenation of cinnamaldehyde even under atmosphere pressure of $H_2$ and room temperature.**

Metal–organic frameworks (MOFs) are emerged as a class of highly promising porous materials, which are synthesized by assembling metal ions with organic ligands in appropriate solvents.[1] Owing to their superior properties including diverse chemical compositions, large surface areas, and permanent porosity, MOFs have potential applications in a wide range of fields such as catalysis,[2] gas storage,[3] separation,[4] and sensing.[5] Over the past decades, most of the research efforts have been focused on preparing new MOF structures and studying their application in gas storage and separation.[6] More recently, the utilizations of MOFs as support for metal nanoparticles have attracted tremendous attention. There have been extensive efforts to fabricate metal nanoparticles (MNPs) on MOFs to obtain the properties that are hardly achieved by their individual parts.[7]

MNPs@MOF composites can be synthesized by using MOFs as templates to generate MNPs or by building MOF structures around preformed MNPs.[8] The latter approach[9] has recently attracted increasing attention as it could avoid the general problems facing the former method, such as aggregation of MNPs on the external surface and damage to the MOF structures during the post-reduction process. Moreover, it could allow a well control of the size, composition, and morphology of the incorporated MNPs.[10] The assembling process generally requires two steps, comprising synthesis of MNPs and then growth of MOF around the surface of pre-synthesized MNPs. Meanwhile, in order to restrict MNPs from aggregation during the MOF assembling process, certain surfactants, capping agents or even ions are often required for the stabilization of the pre-synthesized MNPs. However, such stabilizing agents are difficult to be fully eliminated from the final MNPs@MOF composites, which may have a negative effect on the catalytic efficiencies of MNPs.

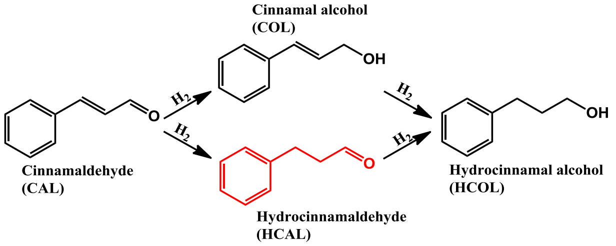
In view of the considerable time and energy consumption in previously reported two-step synthetic procedures, and from the viewpoint of catalysis, it is of great desire to exploit a new methodology for one-pot synthesis of MNPs@MOF composites under stabilizing agent-free conditions. In this regard, the recent work by Tang and co-workers is noteworthy, which reports a PVP assisted one-pot method for the preparation of core–shell Au@MOF-5 composite that can be used as highly selective sensor for $CO_2$ in gas mixtures.[11] To the best of knowledge, however, one-pot synthesis of MNPs@MOF composites without the assistance of any stabilizing agents has not been proposed to date.

Herein, we report, for the first time, a facile one-pot route for the synthesis of Pd@MOF composites without the assistance of any stabilizing agents. The proposed methodology allows the incorporation of highly dispersed metal nanoparticles with surfactant-free surface on MOFs in one step, which could reduce the production cost for ease of scale-up preparation while improve the performance for advanced catalysts. Different from the previous two-step procedure, this one-pot synthetic method is achieved by directly dissolving the precursors of Pd (*i.e.*, $Pd(NO_3)_2$) and MOF (*i.e.*, $ZrCl_4$ and 2,2'-bipyridine-5,5'-dicarboxylic acid) with the reducing agent (*i.e.*, ammonia borane, $NH_3BH_3$) in N,N-dimethylformamide (DMF). This protocol takes advantage of the strong coordinating ability of 2,2'-bipyridine moieties in the organic ligand to palladium, which could stabilize palladium NPs during the MOF assembling process, allowing the hetero-nucleation of MOF on the surface of Pd NPs. The as-prepared Pd@MOF composites exhibited high chemoselectity and activity in the hydrogenation of cinnamaldehyde, showing no reduced catalytic activity even after a number of uses.



**Scheme 1** One-pot synthesis of Pd@MOF**1**.

UiO-67 is a MOF constructed by $[Zr_6O_4(OH)_4(CO_2)_{12}]$ clusters linked with biphenyldicarboxylate (bpdc).[12] Recently, it was reported that the bpdc linker could be replaced with 2,2'-bipyridine-5,5'-dicarboxylate (bpydc), without altering the MOF structure.[13] Considering that the 2,2'-bipyridine moiety on bpydc linker can efficiently stabilize palladium NPs,[14] here we chose $H_2$bpydc as ligand for the one-pot assembling of Pd@MOF**1**. The Pd@MOF**1** was prepared from a mixture containing a 1:1.4 molar ratio of $ZrCl_4$ to $H_2$bpydc in 30:1 v:v DMF:HCl solvent, with the simultaneous addition of palladium precursors and reducing agents (Scheme 1).



**Scheme 2** Reaction pathways in the hydrogenation of cinnamaldehyde.

The synthesis condition was modulated and the as-prepared MOF composites were subsequently used as catalysts for the hydrogenation of cinnamaldehyde (CAL) to evaluate the catalytic activity, selectivity, and reusability. The hydrogenation of cinnamaldehyde, as depicted in Scheme 2, may lead to various products such as cinnamal alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamal alcohol (HCOL), depending on the active metal, solvent, and promoter used in the reaction.[15] Palladium is one of the most active and selective catalysts for the hydrogenation of CAL to HCAL in conventional organic solvents.[16] Although tremendous progresses have been made in this field, the 100% selective hydrogenation of CAL to HCAL is still quite difficult.

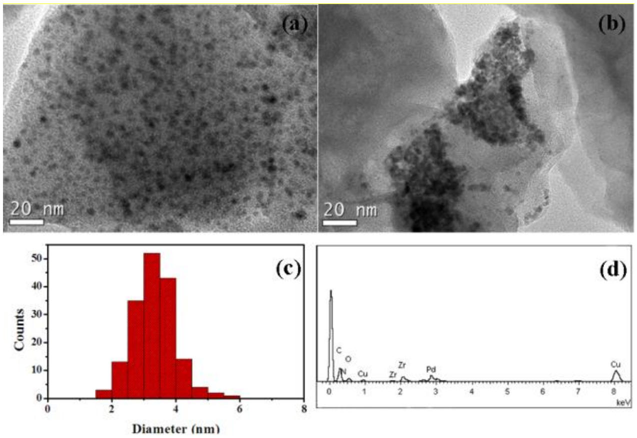


**Fig. 1** (a) TEM image of 2.0% Pd@MOF**1**, (b) TEM image of 2.0% Pd@MOF**2**, (c) corresponding size distribution of Pd nanoparticles of 2.0% Pd@MOF**1**, and (d) the EDX pattern of 2.0% Pd@MOF**1**.

By finely tuning the reaction conditions, the formation rates of Pd NPs and UiO-67 in the mixed solution could be adjusted effectively. From a screening of different kinds of palladium precursors and reducing agents, the combination of $Pd(NO_3)_2$ with $NH_3BH_3$ was found to be the most effective, giving the MOF composite with the highest hydrogenation activity (Table S1). The addition of different amount of $NH_3BH_3$ significantly affected the catalytic activity of Pd@MOF**1**. The activity of Pd@MOF**1** increased gradually when the quantity of $NH_3BH_3$ was increased from 5 mg to 40 mg, and a maximum activity was obtained on the MOF composite prepared with 40 mg of $NH_3BH_3$ (Table 1, entries 1-5). However, when the amount of $NH_3BH_3$ was further increased to 80 mg, the resultant MOF composite gave no catalytic activity. The results pointed to the optimum Pd reducing rate that 40 mg of $NH_3BH_3$ could offer. When the $NH_3BH_3$ amount was less than 40 mg, the concentration of the reducing agent was not sufficient to fully reduce Pd precursors to metallic Pd. However, when the reductant quantity was enhanced to 80 mg, the reduction of Pd precursors was too fast to be well stabilized by the bpydc linkers to yield aggregated Pd NPs with a low reactivity (Figure S1). In the absence of any reducing agent, the obtained composite showed no catalytic activity, implying that Pd(0) was the active site for the hydrogenation transformation under the investigated reaction conditions.

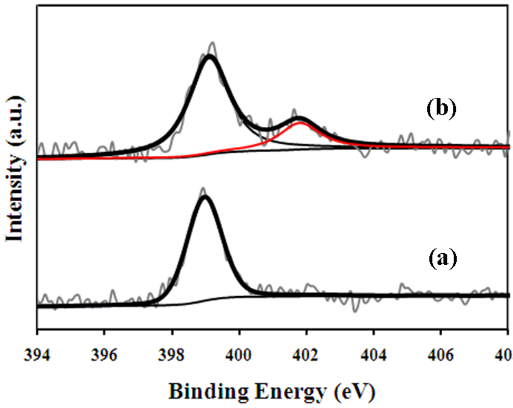


**Fig. 2** XPS spectra of the N 1s region for (a) MOF**1**, and (b) 2.0% Pd@MOF**1**.

The synthesis process can be visibly monitored by the evolution of the solution color. When $NH_3BH_3$ was added to the mixture, the color of the solution quickly changed from light-yellow to dark within a few seconds, indicating that Pd(II) was reduced to Pd(0) NPs. It was found that when Pd NPs were formed, $H_2$bpydc would tend to adsorb on the surface of Pd to stabilize Pd NPs against aggregation due to its strong affinity to Pd (see XPS characterization as described below). Subsequently, $ZrCl_4$ was assembled with $H_2$bpydc absorbed on the surface of Pd NPs to form the MOF, achieving the encapsulation of Pd NPs in UiO-67. Fig. 1a showed that all the Pd NPs were homogeneously distributed in the MOF network, with a mean size of 3.2 nm. No apparent aggregation was observed in the TEM images, indicating a high dispersion of Pd NPs. EDS analysis confirmed the presence of Pd in the Pd@MOF**1**. For comparison, biphenyldicarboxylic acid ($H_2$bpdc) was used as ligand instead of $H_2$bpydc to yield Pd@MOF**2** under similar preparation conditions. However, a serious aggregation of Pd NPs was observed on Pd@MOF**2** (Fig. 1b). The comparison implied that 2,2'-bipridine moiety on $H_2$bpydc played an important role in the assembling process for the stabilization and encapsulation of Pd NPs.

In order to verify the interaction between Pd atoms and bpydc, we performed X-ray photoelectron spectroscopy (XPS) analysis on MOF**1** and Pd@MOF**1**. The parent MOF**1** exhibited one N 1s peak at ca. 399.1 eV (Fig. 2a) that could be related to un-coordinated bipyridinic nitrogen. A new N 1s peak at 401.9 eV was observed for the Pd@MOF**1** material (Fig. 2b), which was shifted by ca. 1.8 eV toward higher binding energies compared with that of un-coordinated bipyridinic nitrogen. Such shifts reflected a decreased in the electron density of N, suggesting a strong coordination between the bpydc moieties and Pd atoms in the Pd@MOF**1**. The XPS results confirmed that a small amount of the uncoordinated bpydc units were bonded to Pd in the Pd@MOF**1**. In addition, as shown in Fig. S2, the Pd@MOF**1** sample exhibited a Pd 3d5/2 band at ca. 335–336 eV, typical of Pd metal, indicating that the Pd(II) cations were transformed to Pd(0) after reduction by $NH_3BH_3$.

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It is noteworthy that the apparently different morphology of Pd NPs between the Pd@MOF**1** and Pd@MOF**2** composites resulted in distinct activities and selectivites in the hydrogenation of CAL to HCAL. As showed in Table 1, Pd@MOF**1**-40 showed 100% yield to HCAL, however, Pd@MOF**2**-40 gave only 75% conversion of CAL with 65% selectivity to the desired product under identical conditions (entries 2 and 7).

**Table 1.** Results of hydrogenation of cinnamaldehyde (CAL).[a]

| Entry | Catalysts [b] | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|---|
| | | | HCAL | HCOL | COL |
| 1 | 2.0% Pd@MOF**1**-80 | <1 | 99 | 1 | 0 |
| 2 | 2.0% Pd@MOF**1**-40 | 100 | 100 | 0 | 0 |
| 3 | 2.0% Pd@MOF**1**-20 | 75 | 79 | 21 | 0 |
| 4 | 2.0% Pd@MOF**1**-10 | 85 | 67 | 33 | 0 |
| 5 | 2.0% Pd@MOF**1**-5 | 8 | 99 | 1 | 0 |
| 6 | 2.0% Pd@MOF**1**-0 | 0 | 0 | 0 | 0 |
| 7 | 2.0% Pd@MOF**2**-40 | 75 | 65 | 35 | 0 |
| 8 | 0.5% Pd@MOF**1**-40 | 72 | 92 | 8 | 0 |
| 9 | 1.0% Pd@MOF**1**-40 | 97 | >99 | <1 | 0 |
| 10 | 4.0% Pd@MOF**1**-40 | 90 | 99 | 1 | 0 |
| 11 | Reused 2.0% Pd@MOF**1**-40 (five uses) | 99 | 100 | 0 | 0 |

[a] Reaction conditions: cinnamaldehyde (0.1 mmol), catalyst (Pd 1 mol%), THF (2 mL), 1 atm $H_2$, 25 °C, 6 h. [b] The prepared Pd@MOF composite is denoted as Pd@MOF-x, where x indicates the amount of $NH_3BH_3$ (mg) added in the solution.

As measured by atomic absorption spectroscopy (AAS), we could achieve different Pd loadings (*e.g.*, 0.5, 1.0, 2.0, and 4.0 wt%) by adding different amount of Pd precursor to the starting materials for the MOF composites. It is interesting to note that the actual loadings were identical to the calculated values. Thus, the proposed strategy could facilitate the accurate control of Pd loading on the MOF.

The powder X-ray diffraction (PXRD) patterns of the samples with different Pd loadings matched well with that simulated from the single-crystal structure, confirming the formation of UiO-67 type structures (Figs. S3 and S4). The absence of a Pd diffraction pattern could be related to the low Pd contents in the materials. All of the obtained Pd@MOF**1** samples were characterized by $N_2$ adsorption at 77 K, and the results are summarized in Fig. S5 and Table S2. As the loading of Pd increased, the corresponding surface area of Pd@MOF**1** decreased, probably due to the pore filling by the doped Pd NPs in the composites. The thermogravimetric analysis (TGA) curve of 2.0% Pd@MOF**1** revealed that the structure of Pd@MOF**1** was thermally stable up to 450 °C under $N_2$ atmosphere (Fig. S6).

All the Pd@MOF**1**-40 samples with different Pd loadings were also applied in the hydrogenation of CAL, and the results are showed in Table 1 (entries 2, 8-10). Results of the hydrogenation of CAL pointed to an optimized performance of 2.0% Pd@MOF**1**-40, which provided a quantitative conversion of CAL to HCAL at 25 °C within 6 h (entry 2). It should be noted that our catalytic system represents a rare example for the selective hydrogenation of CAL with 100% selectivity for HCAL under atmosphere pressure of $H_2$ and room temperature. Considering the adsorption of substrate on the catalyst will significantly influence the catalytic reaction, we speculate that aromatic ligands of MOF**1** would strengthen the adsorption of aromatic rings of CAL *via* π,π-stacking interaction. So CAL would be likely to diffuse into the pore of Pd@MOF**1** in the direction of aromatic ring. This will benefit the adsorption of the C=C bond on the doped Pd surface due to its close distance to the aromatic ring of CAL, thus promote the preferential hydrogenation of C=C bond over C=O bond.

We further investigated the hydrogenation of different cinnamaldehydes**.** The Pd@MOF**1** catalyst was highly active and extremely selective for the hydrogenation of the substituted cinnamaldehydes (Table S3). Cinnamaldehydes of various electronic characters all reacted smoothly (Table S3, entries 1–3). In general, electron-deficient cinnamaldehydes exhibited higher activity than electron-rich ones. Notably, the sterically hindered 2-methoxycimnamaldehyde also worked well and afforded the corresponding product in 98% yield.

Pd@MOF**1** could be easily recovered by centrifugation after removing the supernatant and washing with THF. The recovered catalyst was subsequently reused for a next run under identical conditions with fresh reagents. The catalyst showed no appreciable reduction of activity even after five runs (Table 1, entry 11). PXRD patterns of the used catalyst suggest that the structural integrity of the MOF composite was mostly maintained after the catalytic reactions (Fig. S3). The heterogeneous nature of the Pd@MOF**1** was verified by hot filtration experiment at approximately 19% conversion, which showed that the isolated solution did not exhibit any further reactivity. These findings were consistent with AAS experiments for which no Pd traces (below the detection limit) were found in the reaction solution. Moreover, the Pd loading of the reused material was almost the same as the fresh one. These results indicated that the loss of palladium species was negligible and a truly heterogeneous hydrogenation reaction was taken place on the catalyst surface.

Moreover, the one-pot synthesis method developed in this work is likely a general technique for the preparation of other catalytically active metal@MOF**1** composites, for example, Au@MOF**1** and Pt@MOF**1** (Fig. S7 and Table S4).

In summary, we have developed, for the first time, a novel, facile, and effective methodology for one-pot synthesis of Pd@MOF composites. This strategy features the utilization of MOF ligand for the stabilization of Pd NPs during the encapsulation of Pd NPs within MOF. No additional stabilizing agent was needed here thus could allow the incorporation of metal nanoparticles with surfactant-free surface (a property important for catalysis applications). The as-synthesized Pd@MOF composite was highly active in the selective hydrogenation of cinnamaldehyde, achieving 100% yield to hydrocinnamaldehyde under atmosphere pressure of $H_2$ and room temperature. Moreover, the catalyst was stable and reusable, showing no reduced catalytic activity even after a number of uses. The achieved success in the one-pot synthesis of Pd@MOF composites may pave the way to practical application of metal-loaded MOF materials due to its facile handling, reduced production cost, and ease of up-scaling.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [experimental details, catalysts characterization, and additional reaction results]. See DOI: 10.1039/c000000x/

1 (a) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444; (b) M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343; (c) O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr,

S. T. Nguyen, A. Ö. Yazaydın and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016.

2 (a) T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982; (b) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 5750; (c) J. Gascon, A. Corma, F. Kapteijn and F. X. Llabrés i Xamena, *ACS Catal.*, 2014, **4**, 361.

3 (a) Y. W. Li and R. T. Yang, *J. Am. Chem. Soc.*, 2006, **128**, 726; (b) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782; (c) T. A. Makal, J. R. Li, W. Lu and H. C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761.

4 (a) A. L. Dzubak, L. C. Lin, J. Kim, J. A. Swisher, R. Poloni, S. N. Maximoff and L. Gagliardi, *Nat. Chem.*, 2012, **4**, 810; (b) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954; (c) S. Chaemchuen, N. A. Kabir, K. Zhou and F. Verpoort, *Chem. Soc. Rev.*, 2013, **42**, 9304; (d) Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna and J. R. Long, *Science*, 2013, **340**, 960.

5 (a) Z. Hu, B. J. Deiberta, J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.

6 (a) F. Vermoortele, M. Maes, P. Z. Moghadam, M. J. Lennox, F. Ragon, M. Boulhout, S. Biswas, K. G. M. Laurier, I. Beurroies, R. Denoyel, M. Roeffaers, N. Stock, T. Düren, C. Serre and D. E. De Vos, *J. Am. Chem. Soc.*, 2011, **133**, 18526; (b) B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Yu Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412.

7 (a) J. Juan-Alcañiz, J. Gascon and F. Kapteijn, *J. Mater. Chem.*, 2012, **22**, 10102; (b) H. R. Moon, D.W. Limb and M. P. Suh, *Chem. Soc. Rev.*, 2013, **42**, 1807; (c) Q. Zhu and Q. Xu, *Chem. Soc. Rev.* 2014, **43**, 5468; (d) L. Chen, H. Chen, R. Luque and Y. Li, *Chem. Sci.*, 2014, DOI: 10.1039/c4sc01847h.

8 (a) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2012, **41**, 5262; (b) Y. Liu and Z. Tang, *Adv. Mater.*, 2013, **25**, 5819; (c) M. Meilikhov, K. Yusenko, D. Esken, S. Turner, G. Van Tendeloo and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2010, 3701; (d) D.-W. Lim, J. W. Yoon, K. Y. Ryu and M. P. Suh, *Angew. Chem. Int. Ed.*, 2012, **51**, 9814; (e) J. Hermannsdörfer, M. Friedrich, N. Miyajima, R. Q. Albuquerque, S. Kümmel and R. Kempe, *Angew. Chem. Int. Ed.*, 2012, **51**, 11473; (f) B. Yuan, Y. Pan, Y. Li, B. Yin and H. Jiang, *Angew. Chem. Int. Ed.*, 2010, **49**, 4054; g) H. Liu, G. Chen, H. Jiang, Y. Li and R. Luque, *ChemSusChem.*, 2013, **5**, 1892; (h) A. Aijaz, T. Akita, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 16356; (i) A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama and Q. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 13926; (j) C. Zlotea, R. Campesi, F. Cuevas, E. Leroy, P. Dibandjo, C. Volkringer, T. Loiseau, G. Férey and M. Latroche, *J. Am. Chem. Soc.*, 2010, **132**, 2991; (k) B. W. Jacobs, R. J. T. Houk, M. R. Anstey, S. D. House, I. M. Robertson, A. A. Talinc and M. D. Allendorf, *Chem. Sci.*, 2011, **2**, 411.

9 (a) G. Lu, S. Z. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Y. Qi, Y. Wang, X. Wang, S. Y. Han, X. G. Liu, J. S. DuChene, H. Zhang, Q. C. Zhang, X. D. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. H. Yang, J. T. Hupp and F. W. Huo, *Nat. Chem.*, 2012, **4**, 310; (b) Y. Liu, W. Zhang, S. Li, C. Cui, J. Wu, H. Chen and F. Huo, *Chem. Mater.*, 2014, **26**, 1119; (c) W. Zhang, G. Lu ,C. Cui, Y. Liu, S. Li, W. Yan, C. Xing, Y. Robin Chi, Y. Yang and F. Huo, *Adv. Mater.*, 2014, **26**, 4056; (d) K. Khaletskaya, J. Reboul, M. Meilikhov, M. Nakahama, S. Diring, M. Tsujimoto, S. Isoda, F. Kim, K. Kamei, R. A. Fischer, S. Kitagawa and S. Furukawa, *J. Am. Chem. Soc.*, 2013, **135**, 10998; (e) T. Tsuruoka, H. Kawasaki, H. Nawafune and K. Akamatsu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 378; (f) P. Wang, J. Zhao, X. Li, Y. Yang, Q. Yang and C. Li, *Chem. Commun.*, 2013, **49**, 3330.

10 (a) M. Zhao, K. Deng, L. He, Y. Liu, G. Li, H. Zhao and Z. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 1738; (b) C.-H. Kuo, Y. Tang, L.-Y. Chou, B. T. Sneed, C. N. Brodsky, Z. Zhao and C.-K. Tsung, *J. Am. Chem. Soc.*, 2012, **134**, 14345.

11 L. He, Y. Liu, J. Liu, Y. Xiong, J. Zheng, Y. Liu and Z. Tang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3741.

12 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.

13 (a) J. B. DeCoste, G. W. Peterson, H. Jasuja, T. G. Glover, Y. Huang and K. S. Walton, *J. Mater. Chem. A*, 2013, **1**, 5642; (b) M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449; (c) L. Li, S. Tang, C. Wang, X. Lv, M. Jiang, H. Wu and X. Zhao, *Chem. Commun.*, **2014**, **50**, 2304.

14 (a) G. Petruccia, W. Oberhauserb, M. Bartolia, G. Giachia, M. Frediania, E. Passagliac, L. Capozzolid and L. Rosi, *Appl. Catal. A-Gen.*, 2014, **469**, 132; (b) M. Crespo-Quesada, R. R. Dykeman, G. Laurenczy, P. J. Dyson and L. Kiwi-Minsker, *J Catal.*, 2011, **279**, 66.

15 (a) X. Yang, D. Chen, S. Liao, H. Song, Y. Li, Z. Fu and Y. Su, *J Catal.*, 2012, **291**, 36; (b) K. Sun, Y. Hong, G. Zhang and B. Xu, *ACS Catal.*, 2011, **1**, 1336; (c) B. Wu, H. Huang, J. Yang, N. Zheng and G. Fu, *Angew. Chem. Int. Ed.*, 2012, **51**, 3440; (d) K. R. Kahsar, D. K. Schwartz and J. W. Medlin, *J. Am. Chem. Soc.*, 2014, **136**, 520; (e) G. Kennedy, L. R. Baker and Gabor A. Somorjai, *Angew. Chem. Int. Ed.*, 2014, **53**, 3405.

16 (a) H. Mao, H. Yu, J. Chen and X. Liao, *Sci. Rep.*, 2013, **3**, 2226; (b) G. Kong, S. Ou, C. Zou and C. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 19851; (c) H. Kochkar, M. Aouine, A. Ghorbel and G. Berhault, *J. Phys. Chem. C*, 2011, **115**, 11364.