Catalysis Communications 59 (2015) 92–96

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Ag–Cu–BTC prepared by postsynthetic exchange as effective catalyst for selective oxidation of toluene to benzaldehyde

Zhiguo Sun [a,b], Gang Li [a,*], Yue Zhang [a], Hai-ou Liu [a], Xionghou Gao [b]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, No. 2 Ling-gong Road, Dalian 116024, China
[b] Lanzhou Petrochemical Research Center, Petrochemical Research Institute, PetroChina Company, Ltd., Lanzhou 730060, China

ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 24 September 2014
Accepted 26 September 2014
Available online 5 October 2014

Keywords:
Metal-organic frameworks
Postsynthetic exchange
Ag–Cu–BTC
Toluene selective oxidation
Benzaldehyde

ABSTRACT

A mixed-node MOF catalyst Ag–Cu–BTC was prepared by postsynthetic exchange (PSE) method. It is believed that PSE method can realize isomorphous replacement of Ag ion to framework Cu ion in Cu–BTC successfully. The catalytic performance of Ag–Cu–BTC was investigated via selective oxidation of toluene to benzaldehyde by molecular oxygen in the absence of solvent and initiator. This catalyst exhibits good catalytic performance: on the premise of keeping highly selective catalysis of Cu–BTC for toluene oxidizing to benzaldehyde, the introduction of Ag (Ag content is 2.76 wt.%) can promote toluene conversion from 6.5% to 12.7%.

1. Introduction

The selective oxidation of hydrocarbons into useful oxygenated chemicals is an important family of chemical transformations [1–3]. Among them, the direct oxidation of toluene by oxygen to produce benzaldehyde is an attractive process. Benzaldehyde is a versatile intermediate in the manufacture of perfumes, pharmaceuticals, dyes and so on [4–6]. Commercially, benzaldehyde is mainly produced by the chlorination of toluene followed by the hydrolysis process, which generates large amounts of toxic acidic/basic discard solution, leading to equipment corrosion and environmental pollution. Even worse, the benzaldehyde produced by this route is not qualified to synthesize some high-quality compounds such as perfumes or pharmaceuticals because the product contains chlorine [7,8]. Therefore, there is a clear need to develop selective oxidation of toluene as an alternative route to produce benzaldehyde. There have been many attempts to find an effective heterogeneous catalyst for this reaction. It was reported that Cu–Fe/γ-Al_2O_3 catalyzed solvent-free toluene oxidation with O_2 to produce benzaldehyde with 85.9% selectivity at 7.3% conversion in the presence of pyridine(463 K, 1.0 MPa and 2 h) [4]. Au–Pd nanoparticles supported on carbon gave 63.4% selectivity to benzaldehyde at 1.5% conversion (433 K, 1.0 MPa and 7 h) [6]. Obviously, a catalyst with high selectivity and improved activity for this process is greatly demanded.

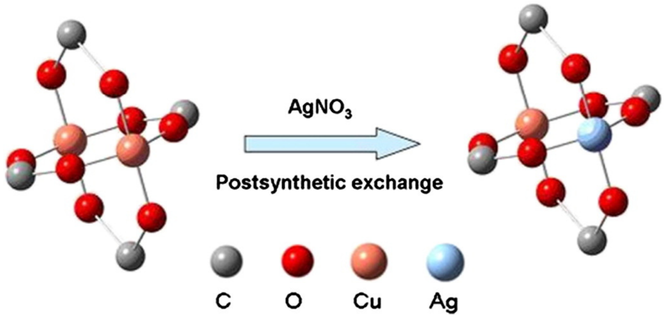
Recently, metal-organic frameworks (MOFs) have generated substantial attention for the use in catalysis [9,10]. They are porous materials composed of metal nodes connected by organic ligands, allowing for great chemical and structural diversity. These characters as well as functionizable crystalline framework provide multiple opportunities to create desirable active sites and determine MOFs as excellent candidates for catalysis application [11–13]. Among reported MOF catalytic systems, node metal as catalytic center is the most common case [14–16]. These node metals provide uniform, high density and non-leaching catalytic centers and exhibit versatile catalytic properties. However, the investigations mainly focus on single-node MOF catalysts and the explorations of mixed-node MOF catalysts are very limited so far. The development of mixed-node MOF catalyst is of special interest because the incorporation of two or more kinds of metal ions can add different functionalities. A mixed-node MOF may realize more complicated catalysis such as multiple catalysis or cooperative catalysis.

A useful strategy to prepare mixed-node MOF is to use different metal ions in the synthetic system [17]. But this method is not widely applicable and needs strict control to synthetic conditions, since the addition of another metal ion may affect the formation of target structure. An alternative strategy is to substitute some of the metal nodes in a pre-formed MOF with another metal ion by postsynthetic exchange (PSE) [18]. Unlike other porous materials such as zeolites, mesoporous silicas and porous carbons, one distinct feature of MOFs is their excellent postfunctionalization ability [19]. A variety of functional groups can be introduced to MOFs through postsynthetic approaches, such as postsynthetic modification (PSM) [20] and postsynthetic deprotection (PSD) [21]. PSE is a recently reported postsynthetic approach to

---

* Corresponding author. Tel./fax: +86 411 84986113.
E-mail address: liganghg@dlut.edu.cn (G. Li).

http://dx.doi.org/10.1016/j.catcom.2014.09.047
1566-7367/



Scheme 1. The preparation of Ag–Cu–BTC.

produce functionalized MOFs [22]. It denotes a process that the node metals or ligands in a MOF crystallite can be readily replaced with other ones through an exchange fashion while keeps the structure of MOF intact. This approach provides a generally applicable means to prepare mixed-node MOFs, in which the proportions of metals can be adjusted.

Herein, we report a mixed-node MOF denoted as Ag–Cu–BTC, which was prepared by PSE method. The catalytic performance of this material was investigated via selective oxidation of toluene to benzaldehyde by molecular oxygen in the absence of solvent and initiator.

2. Experimental

2.1. Catalyst preparation

The nitrates were purchased from Sinopharm Chemical Reagent Company, Ltd. Trimesic acid was purchased from J&K Chemical Company. All the chemicals were used as received without further purification.

MOFs were synthesized and activated according to the literatures [23–26]. Ag–Cu–BTC was prepared through a PSE method. Typically, 0.064 g AgNO$_3$ was dissolved in the mixture of 48 mL deionized water and 48 mL ethanol in 125 mL stainless steel autoclave with a polytetrafluoroethylene liner. 0.4 g prepared Cu–BTC was added into and the autoclave was put in a 358 K oven. The ion exchange was carried out for 1 day. Then, the reactor was cooled down to room temperature. After filtration, the cyan solid was washed with excess ethanol and deionized water. Finally, the product was dried under vacuum at 373 K over the night (Scheme 1).

2.2. Catalyst characterization

The element contents of the samples were determined by inductively coupled plasma (ICP) on Optima 2000DV instrument. Powder X-ray diffraction (XRD) patterns were employed to identify the structures of prepared samples. The XRD patterns were recorded on Rigaku D/Max 2400 diffractometer employing Cu Kα radiation. Raman spectra were recorded using DXR micro Raman spectrometer from Thermo Scientific Company. The 532 nm wavelength laser source was adopted to investigate the M–O bonding situation in MOFs. X-ray photoelectron spectroscopy (XPS) was conducted to determine the states of elements in material using a Thermo ESCALAB 250 X-ray photoelectron spectrometer. Al–Kα acted as light source and Cls (284.6 eV) was used to correct XPS peaks of other elements. The scanning electron microscopy (SEM) images were obtained on a NOVA NANOSEM 450 field-emission scanning electron microscopy using a 20 kV energy source under vacuum. Oxford energy dispersive X-ray analysis (EDAX) and Inca software were used to determine elemental mapping of particle surfaces at a working distance of 5 mm. The BET surface areas of the samples were measured by N$_2$ physical adsorption–desorption at 77 K on a Quantachrome AUTOSORB-1 apparatus.

2.3. Catalytic test

Typically, the selective oxidation of toluene was carried out in a 100 mL stainless steel autoclave with a polytetrafluoroethylene liner. 10 mL toluene and 0.1 g solid catalyst were added into the reactor. The autoclave was charged with 1.0 MPa oxygen, stirred and heated to reactive temperature and kept on reacting for 4 h. Afterward, the reactor was cooled down to room temperature and the pressure was released slowly. The products were diluted with acetone and transferred to a 50 mL volumetric flask totally. After enough mixing, the sample was analyzed by Agilent GC-6890 N (HP-5 capillary column, Flame Ionization Detector).

For the recyclability tests, the reactions were performed under the same reaction conditions, except using the recovered catalyst. To study the leaching of exchanged ion during the reaction, the reaction mixture was treated by centrifugation and the solution was analyzed by ICP.

3. Results and discussion

3.1. Catalytic performances of MOFs with different node metals

In order to investigate the catalytic performances of different node metals for toluene selective oxidation, MOFs prepared by trimesic acid (H$_3$BTC) coordinated with different metal ions (Cr, Al, Fe, Cu) were taken as catalysts. The concentrations of Cr, Al, Fe, and Cu in the samples are 19.53, 16.15, 21.64 and 29.82 wt.%, respectively. These data imply that the amounts of active centers are enough and the catalytic performance of sample is mainly determined by the nature of node metal. The reaction results are listed in Table 1 (entry 2 to 5). Contrasting the catalytic performances of MOFs with different node metals, we can see

Table 1
The catalytic performances of different catalysts in toluene selective oxidation.[a]

Entry	Catalyst	Conv./%	Benzyl alcohol select./%	Benzaldehyde select./%	Benzoic acid select./%	Others/%
1	None	4.2	15.8	47.6	33.7	2.9
2	Cr–BTC	12.4	0	49.5	47.5	3.0
3	Al–BTC	9.0	3.5	53.1	41.8	1.6
4	Fe–BTC	5.9	17.0	58.4	24.3	0.3
5	Cu–BTC	6.5	0	99.5	0	0.5
6	AgNO$_3$	20.5	41.8	41.4	13.6	3.2
7	Ag–Cu–BTC(0.69)[b]	9.8	0	99.1	0.5	0.4
8	Ag–Cu–BTC(2.76)[b]	12.7	0	99.0	0.7	0.3
9	Ag–Cu–BTC(4.15)[b]	13.0	0	98.2	1.1	0.7
10	Ag–Cu–BTC(4.15)[b,c]	20.1	0	90.6	7.9	1.5

[a] Reactive condition: catalyst 0.1 g; O$_2$ pressure 1.0 MPa; reaction temperature 433 K; reaction time 4 h.
[b] Data in bracket are weight percentage contents of Ag.
[c] The test was performed for 8 h while other conditions kept unchanged.

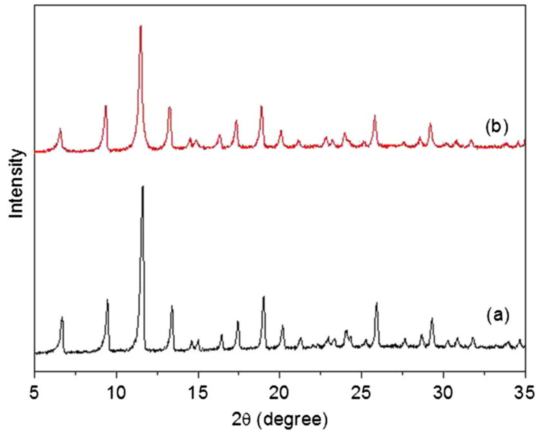


Fig. 1. Powder XRD patterns of samples: (a) Cu–BTC; and (b) Ag–Cu–BTC.

Table 2
Electronic binding energies of various Ag species.[a]

Orbit	Ag	Ag_2O	AgO	Ag–Cu–BTC
Ag $3d_{3/2}$	373.4–374.2	373.9	–	374.9
Ag $3d_{5/2}$	367.9–368.4	367.7–368.4	367.3–368.0	368.8

[a] The data of Ag, Ag_2O and AgO come from NIST XPS Database.

that node metals have huge influence on toluene selective oxidation. When Cr–BTC acts as catalyst, the conversion rate of toluene is highest among the single-node MOF catalysts. However, the products are mixture of benzaldehyde and benzoic acid, leading to the selectivity of benzaldehyde is only 49.5%. For Cu–BTC catalyst, although the conversion rate of toluene is not high, the selectivity of benzaldehyde can reach to 99.5%. The exploitation of high selective chemical reaction can reduce the waste of raw material, save energy consumption in products separation and protect environment. Therefore, we take Cu–BTC as main body catalyst for selective oxidation of toluene to benzaldehyde and explore method to improve its activity. Then, Ag–Cu–BTC was prepared and its catalytic performance in toluene selective oxidation to benzaldehyde was studied.

3.2. Characterization of Ag–Cu–BTC

The most direct means to judge whether Ag was introduced to MOF matrix is elemental analysis. The ICP analysis indicates that the actual Ag content of Ag–Cu–BTC prepared by described method is 2.76 wt.%. In addition, Ag–Cu–BTC was treated with nitric acid and the filtrate was analyzed by ICP. There is no detectable Ag in filtrate discloses that Ag element does not exist in the form of Ag_2O or AgO on the Cu–BTC surface. The XRD patterns were employed to identify the Cu–BTC samples (Fig. 1). The patterns of the Ag–Cu–BTC and Cu–BTC are very similar, which indicates that the ion exchange process is isomorphous replacement and crystal structure of Cu–BTC is kept intact under adopted conditions. No any new peak appears in the pattern of Ag–Cu–BTC, which can exclude the cases that Ag species is existed in new crystal form or loaded on framework in $AgNO_3$ form. Fig. 2A presents Raman spectra of Cu–BTC and Ag–Cu–BTC with different Ag exchange degrees. The most notable change for Ag–Cu–BTC spectra is that a new peak appears at 230 cm^{-1} and the intensity of this peak increases with the Ag exchange degree. This indicates that the peak directly relates to the newly generated Ag species and can be attributed to the characteristic peak of Ag – O bond. Fig. 2B shows high resolution XPS of Ag 3d region for Ag–Cu–BTC. It can be seen that the electron binding energies corresponding to Ag $3d_{3/2}$ and Ag $3d_{5/2}$ photoelectron peaks are 374.9 and 368.8 eV, respectively. These numerical values are bigger than that of common chemical states of Ag element (Table 2). This is owing to the Ag ion in Ag–Cu–BTC which is linked with four oxygen atoms of carboxylic ligands. The oxygen atoms with large electronegativity make share electron pair deviate from Ag ion, which leads to the increase of inner electron binding energy. Scanning electron microscopy and energy dispersed X-ray analysis (SEM-EDAX) also confirmed the presence of both Cu and Ag in Ag–Cu–BTC particle (Fig. 3). The even distribution of Ag element implies that Ag species is located in the crystal lattices of Ag–Cu–BTC. All above results together provide substantial evidence to that Ag–Cu–BTC was prepared successfully.

3.3. Catalytic performance of Ag–Cu–BTC in toluene selective oxidation

The catalytic performances of $AgNO_3$ and Ag–Cu–BTC with different Ag exchange degrees for toluene selective oxidation to benzaldehyde are listed in Table 1 (entry 6 to 10). It can be seen that when $AgNO_3$ is used as catalyst, the conversion rate of toluene is comparatively high, which indicates that Ag ions can boost the activation of toluene. However, the selectivity of benzaldehyde is not satisfactory. When Ag–Cu–BTC acts as catalyst, comparing with Cu–BTC, the conversion of toluene can be greatly improved while the selectivity of benzaldehyde has no obvious decrease. In order to compare selectivity of Ag–Cu–BTC with that of $AgNO_3$ at the similar level of conversion, the conversion rate of toluene was raised to 20.1% by increasing reaction time to 8 h. It was found that the selectivity of benzaldehyde is still above 90%. The BET specific surface areas of Cu–BTC and Ag–Cu–BTC are both $>1000\ m^2/g$ while that of $AgNO_3$ is $<1\ m^2/g$. Big specific surface area means a large

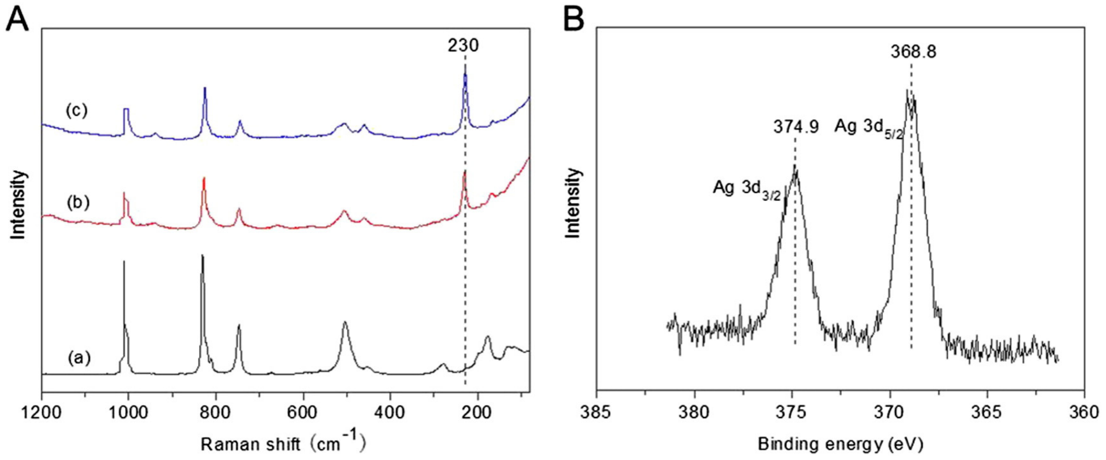


Fig. 2. The Raman spectra of samples (A): (a) Cu–BTC; (b) Ag–Cu–BTC(Ag content 2.76%); (c) Ag–Cu–BTC(Ag content 4.15%) and high resolution XPS of Ag 3d region for Ag–Cu–BTC(B).

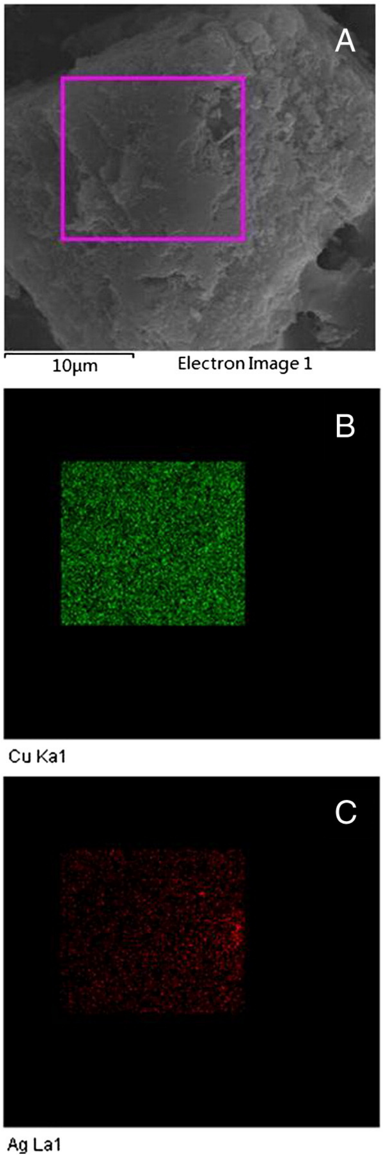


Fig. 3. SEM-EDAX mapping of Ag–Cu–BTC single particle: SEM image (A) and the corresponding elemental distributions of Cu (B, green) and Ag (C, red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

number of accessible active sites. So it can be concluded that single atom activity of Ag is much higher than that of Cu. This may account for the obvious increase of toluene conversion on Ag–Cu–BTC. A small amount of framework Ag ions can promote the conversion of toluene. However, the raise of toluene conversion becomes very slow when Ag exchange degree achieves a certain value. Moreover, the selectivities of by-products also increase with Ag exchange degree of catalyst. So there is an appropriate Ag exchange degree to obtain satisfactory catalytic performance. When Ag content is 2.76 wt.%, the conversion of toluene reaches to 12.7% while the selectivity of benzaldehyde keeps at 99.0% over Ag–Cu–BTC catalyst. The above results demonstrate that the introduction of Ag indeed enhances the catalytic ability of Cu–BTC for toluene selective oxidation to benzaldehyde.

The recyclability is also a vital character for a practical solid catalyst. Other ion exchange catalysts such as ion exchange zeolite and ion exchange resin, usually deactive in reuse since the leaching of exchanged ions. In this work, we examined the recyclability of Ag–Cu–BTC (Ag content is 2.76 wt.%) in toluene selective oxidation by using the recovered catalyst under the same reaction conditions. Fig. 4 reveals that Ag–Cu–BTC exhibits good recyclability: no noticeable decreases of toluene conversion or benzaldehyde selectivity can be observed during 4 cycle run. The ICP analyses can't detect any Ag or Cu in the solution of reaction products. It indicates that Ag–Cu–BTC holds outstanding stability and both framework Cu ions and exchanged Ag ions do not leach out. Ag–Cu–BTC has much better stability than other ion exchanged catalysts because the exchanged ion was introduced to matrix by coordinate bond rather than physical force.

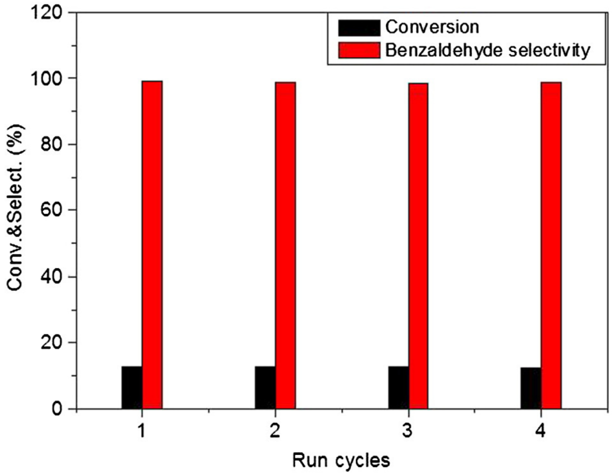


Fig. 4. Recyclability of Ag–Cu–BTC for toluene selective oxidation.

4. Conclusions

In summary, a mixed-node MOF catalyst Ag–Cu–BTC was prepared by PSE method and used in toluene selective oxidation to benzaldehyde. Ag–Cu–BTC exhibits good catalytic performance: on the premise of keeping highly selective catalysis of Cu–BTC, the introduction of Ag greatly promotes toluene conversion. It demonstrates that PSE is a practical and powerful route to develop mixed-node MOF catalysts.

Acknowledgments

The financial support from National Basic Research Program of China (2011CB201301) is gratefully acknowledged.

References

[1] Y. Ishii, S. Sakaguchi, T. Iwahama, Adv. Synth. Catal. 343 (2001) 393–427.
[2] R.K. Grasselli, Top. Catal. 21 (2002) 79–88.
[3] R. Curci, L. D'Accolti, C. Fusco, Acc. Chem. Res. 39 (2006) 1–9.
[4] F. Wang, J. Xu, X.-Q. Li, J. Gao, L.-P. Zhou, R. Ohnishi, Adv. Synth. Catal. 347 (2005) 1987–1992.
[5] J.-G. Lv, Y. Shen, L.-M. Peng, X.-F. Guo, W.-P. Ding, Chem. Commun. 46 (2010) 5909–5911.
[6] L. Kesavan, R. Tiruvalam, M.H. Ab Rahim, M.I. bin Saiman, D.I. Enache, R.L. Jenkins, N. Dimitratos, J.A. Lopez-Sanchez, S.H. Taylor, D.W. Knight, C.J. Kiely, G.J. Hutchings, Science 331 (2011) 195–199.
[7] W. Partenheimer, Catal. Today 23 (1995) 69–158.
[8] L.-H. Jia, S. Zhang, F.-N. Gu, Y. Ping, X.-F. Guo, Z.-Y. Zhong, F.-B. Su, Microporous Mesoporous Mater. 149 (2012) 158–165.
[9] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun. 48 (2012) 11275–11288.
[10] K. Leus, Y.-Y. Liu, P. Van Der Voort, Chem. Rev. 56 (2014) 1–56.
[11] J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450–1459.
[12] A. Corma, H. García, F.X. Llabrés i Xamena, Chem. Rev. 110 (2010) 4606–4655.
[13] M. Ranocchiari, J.A. Bokhoven, Phys. Chem. Chem. Phys. 13 (2011) 6388–6396.
[14] C.N. Kato, M. Hasegawa, T. Sato, A. Yoshizawa, T. Inoue, W. Mori, J. Catal. 230 (2005) 226–236.
[15] Y.K. Hwang, D.-Y. Hong, J.-S. Chang, S.H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, Angew. Chem. Int. Ed. 47 (2008) 4144–4148.
[16] J. Kim, S. Bhattacharjee, K.-E. Jeong, S.-Y. Jeong, W.-S. Ahn, Chem. Commun. (2009) 3904–3906.
[17] S. Nayak, K. Harms, S. Dehnen, Inorg. Chem. 50 (2011) 2714–2716.

[18] A.D. Burrows, CrystEngComm 13 (2011) 3623–3642.
[19] Z.-Q. Wang, S.M. Cohen, Chem. Soc. Rev. 38 (2009) 1315–1329.
[20] S.M. Cohen, Chem. Rev. 112 (2012) 970–1000.
[21] R.K. Deshpande, G.I.N. Waterhouse, G.B. Jameson, S.G. Telfer, Chem. Commun. 48 (2012) 1574–1576.
[22] M. Kim, J.F. Cahill, H.-H. Fei, K.A. Prather, S.M. Cohen, J. Am. Chem. Soc. 134 (2012) 18082–18088.
[23] M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P.L. Llewellyn, J.-H. Lee, J.-S. Chang, S.H. Jhung, G. Férey, Angew. Chem. Int. Ed. 45 (2006) 8227–8231.
[24] T. Loiseau, L. Lecroq, C. Volkringer, J. Marrot, G. Férey, M. Haouas, F. Taulelle, S. Bourrelly, P.L. Llewellyn, M. Latroche, J. Am. Chem. Soc. 128 (2006) 10223–10230.
[25] P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, Chem. Commun. (2007) 2820–2822.
[26] M. Hartmann, S. Kunz, D. Himsl, O. Tangermann, Langmuir 24 (2008) 8634–8642.