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ARTICLE

Preparation and Catalytic Properties of Pd Nanoparticles Supported on Micro-crystal DUT-67 MOFs

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Zr-based MOFs usually feature exceptionally high thermal and chemical stability, which induces that the composite of novel metal and Zr-based MOF exhibits wide industrial application. In this work, we reported the synthesis and characteristic of three different loading (0.3%, 0.5% and 1.0%) Pd nanoparticles supported on micro-crystal DUT-67 MOF. Via the characteristics of SEM, TEM and XPS, it is found that Pd nanoparticles well disperse on the interface of MOFs micro-crystal with the diameter of 3.5 nm, where both dangling organic group and cavity of MOFs play important roles. Furthermore, the measurements of PXRD, IR, TGA and N₂ adsorption confirms both of two composites are very robust. Catalytic properties studies indicate that they both have good catalytic performance with conversion of 99% and selectivity of 89% in the Suzuki coupling reaction. By a series of explorations, we found the best catalytic condition is to use ethanol-water mixed solvent as media, K₂CO₃ as base and at 70 °C. Moreover, they also indicate good catalytic properties with conversion of 99% and selectivity of 99% in the reaction of nitrobenzene hydrogenation, where the appropriate temperature is 60 °C.

Introduction

In the last two decades, Metal-organic frameworks (MOFs) have attracted enormous attentions owing to regular porous structure and potential applications, such as adsorption², separation³, catalysis⁴, luminescence⁵, magnetism⁶ and nonlinear optics⁷. Arguably most notable in this context is the research on heterocatalysis⁸. By design or serendipity, many catalytically-active MOFs were realized, which involves acid catalysis⁹, base catalysis¹⁰ and asymmetric catalysis¹¹. Essentially, active sites are mainly originated from auguring moieties of linking units and unsaturated metal sites. However, owing to coordination geometry requirement of metal ions and changeable coordination geometry of ligands, these congenital active MOFs usually exhibit some huge synthetical challenges, which may hinder the further development of MOFs in industrial applications.

Noble metal nanoparticles (NMNPs) usually show good catalytic performance. As for featuring some dangling organic groups in the interface, MOFs micro-crystals or nano-crystals as good supporter are capable of stabilizing nanosized novel metal clusters¹². Since the first report of Pd/MOF-5 by Fischer¹³, efforts made by many chemists have resulted in a series of studies^{12, 14}, including various MOFs (e.g. MOF-74¹²,

ZIF-8^{14g, 15}, MIL-101¹⁶, MOF-177¹⁷ and et al.) and single or binary metal cluster. Within this context, Zr-based MOFs usually exhibit exceptionally high thermal and chemical stability¹⁸, which promotes them to serve as potential substrates in industrial application. Recently, great attentions were drawn on NMNPs/Zr-MOFs. And these studies only involve two Zr-based MOFs: UIO-66 and UIO-67. DUT-67 prepared by I. Senkovska et. al.¹⁹ is a MOFs with the most largest inner pore of 14.2 Å, which can be regarded as the assemble of Zr₆O₆(OH)₂ building block connecting by thiophenedicarboxylic acid. However, corresponding studies of NMNPs/DUT-67 have never been reported so far.

In this study, we reported the synthesis and characteristic of Pd nanoparticles supported DUT-67 catalyst, where Pd nanoparticles with the diameter of 3.5 nm are well dispersed on the interface of DUT-67 micro-crystal. Catalytic measurements show they exhibit good performance in the reaction of Suzuki coupling and nitrobenzene hydrogenation.

Experimental Details

Structure Characteristic and Property Measurement

All reagents and chemical were purchased from Aladdin and used without further purification. The obtained structure was

performed by X-ray powder diffraction (PXRD) patterns in a Panalytical X-Pert pro diffractometer with Cu-K α radiation. The shapes and morphologies of catalysts were observed by scanning electron microscopy (SEM, Hitachi S4700) and transmission electron microscopy (TEM, Tecnai G2 F30). A thermal gravimetric analyzer (SDT Q600, TA Instruments Co.) was applied to thermogravimetric analysis (TGA), where samples were heated at a rate of 10°C •min⁻¹ from room temperature to 800°C in an ambient atmosphere. X-ray photoelectron spectroscopy (ESCALab220i-XL) were carried out from VG Scientific using 300W Al K α radiation. Fourier transformed infrared (FT-IR) spectrum was tested by a Nicolet 6700 FT-IR spectrometer (Thermo). The surfaces area was accounted from the nitrogen adsorption isothermal were experimented with an Surface properties analyzer instrument (3Flex, Micromeritics). The resultant products were confirmed by Gas Chromatography-Mass Spectrometer (GC/MS, GCT Premier).

Synthesis of DUT-67: DUT-67 were synthesized according to the references, as follows: ZrCl₄ (167mg, 0.5 mmol) solid powder was dissolved in the mixture of DMF (6.25 mL) and NMP (6.25 mL) by sonication for 10 min. Subsequently, 2,5-Thiophenedicarboxylic acid (H₂TDC) (56mg, 0.34 mmol) was added to the mixture and sonicated for 5 min. Then acetic acid (3.5 mL) was added to the solution and further sonicated for 10 min. The resulting mixture was transferred to a 25mL Teflon-lined stainless steel autoclave and heated to 120 °C for 2 days under autogenous pressure. The obtained powder was filtrated and washed several times with DMF and ethanol until the filtrate became colorless. The resultant product was filtered and dried at 80 °C under vacuum for three hours.

Synthesis of Pd/DUT-67: Firstly, as-prepared DUT-67(0.1g) was dissolved in 8mL DMF through sonication for 10min. Meanwhile, different amount PdCl₂ powder (1.0mg/0.01mmol for 0.3%Pd/DUT-67; 1.7mg/0.01mmol for 0.5%Pd/DUT-67; 3.4mg/0.02mmol for 1.0%Pd/DUT-67) were dispersed in another 4mL DMF via stirred in a 25ml beaker. Then, both solution were mixed into a flask and further stirred for 5h. NaBH₄ (12mg for 0.3%Pd/DUT-67, 20mg for 0.5%Pd/DUT-67; 40mg for 1.0%Pd/DUT-67) was dropwise added to the mixture. Finally, the color of solution changed from orange to black. The product was collected by filtration and washed with DMF and diethyl ether for several times. The resultant products were dried under vacuum at 80 °C under vacuum for 3 hours.

Suzuki coupling reaction using Pd/DUT-67 as catalyst: 0.1mmol iodobenzene, 0.6 mmol R-substituted phenylboronic acid and 1 mmol base added was dissolved in a specific solvent (see following discussion). Subsequently, 20mg Pd@DUT-67 was added to the mixture. The catalytic reaction was conducted at 30-80 °C for an hour. The final product was analyzed by GC (FuLi-9790II) with a flame-ionization detector using a weak polarity column (AT.SE-54) .

Nitrobenzene hydrogenation using Pd/DUT-67 as catalyst : All catalytic reactions were carried out for 3 hours in a steel autoclave with 2 bar H₂ and temperature range from 30 to 60 °C. A typical experiment consists of catalyst (20.0 mg) ,

nitrobenzene (0.3 mL) and ethanol (15 mL). The resultant product was identified by GC (FuLi-9790II) with a flame-ionization detector using a weak polarity column (AT.SE-54) .

Results and discussion

Structural characteristic

DUT-67 MOF crystallizes in Fm $\bar{3}m$ space group and exhibits two different inner pores: 14.2 for cuboctahedral cage and 11.6 Å for octahedral cage¹⁹. The whole framework indicates a binodal 8-connected net, which can be regarded as the assemble of Zr₆O₆(OH)₂ unit connecting by TDC²⁻ ligand¹⁹. As shown in Fig. 1, SEM images show polyhedral micro-crystals of DUT-67, where the crystal planes have two different shapes: regular hexagon and square. And in the face, the edge size is about 1 μ m. The phenomenon was well corresponded to the reported article about DUT-67. Furthermore, TEM images indicate two different polyhedral microcrystals feature good crystalline phase.

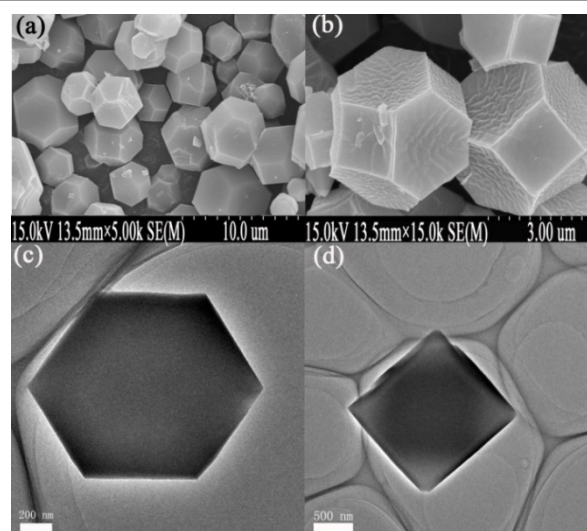


Fig 1. Representative SEM (a-b)and TEM (c-d) images for DUT-67

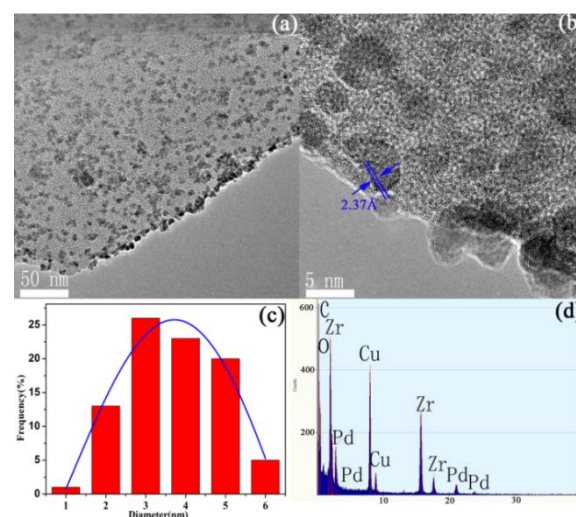


Fig.2. TEM images (a-b), Pd-NPs distribution curve (c) and EDS analysis result (d) for 0.5% Pd/DUT-67

For the Pd NPs-supported DUT-67, we performed 0.3%, 0.5% and 1% ratio loading Pd on DUT-67(see Fig. S1-S3). SEM image of 0.5%Pd@DUT was shown in Fig. S4a. Fig. 2(a-b) shows the TEM images of 0.5%Pd@DUT-67, where most of Pd NPs prefer to well disperse on the crystal planes of DUT-67 than the porous matrices of the framework. It is observed that some Pd NPs concentrate on the edge of micro-crystals, suggesting a chemical adsorption interaction between Pd NPs and the interface of MOFs. From the image of Fig. 2b, we can see the Pd NPs on the interface partially permeate into the cavity of MOFs. Thus, it is concluded that both cavity and interface of MOFs play important roles on the adsorption of Pd NPs. Moreover, lattice fringe of Pd NPs were observed in Fig. 2b, leading to interplanar spacing of 2.37 Å. Accounting more than 100 particles in the TEM images reveals that the average diameter of Palladium is c.a. 3.5 nm (see Fig. 2c). Energy dispersive X-ray spectroscopy (EDS) spectra also confirm the constituent of Pd and Zr element on the DUT-67. To further confirm the chemical state of the loading Pd on the DUT-67, X-Ray photoelectron spectroscopy was carried out. Fig. 3a shows the two peaks of Pd (338.4 and 332.9eV) and Zr (343.9 and 330.3 eV), respectively, which can be assigned to $3d_{3/2}$ and $3d_{5/2}$ of Pd(0), $3p_{1/2}$ and $3p_{3/2}$ of Zr(IV). Thermogravimetric analysis results exhibit that after loading Pd NPs the whole framework maintain original thermal stability (see Fig. 3b). As displayed in Fig. 3c, FT-IR spectras show that there is not obvious difference between them, which also validate the stability after Pd NPs loading. Nitrogen adsorption isotherms before and after Pd NPs loading are shown in Fig.3d. The specific surface area estimated by Brunauer–Emmett–Teller (BET) methods are 967 m²/g for DUT and 301 m²/g for 0.5% Pd/DUT-67, respectively. Obviously, the surface area decreasing after the Pd NPs loading may be attributed to the

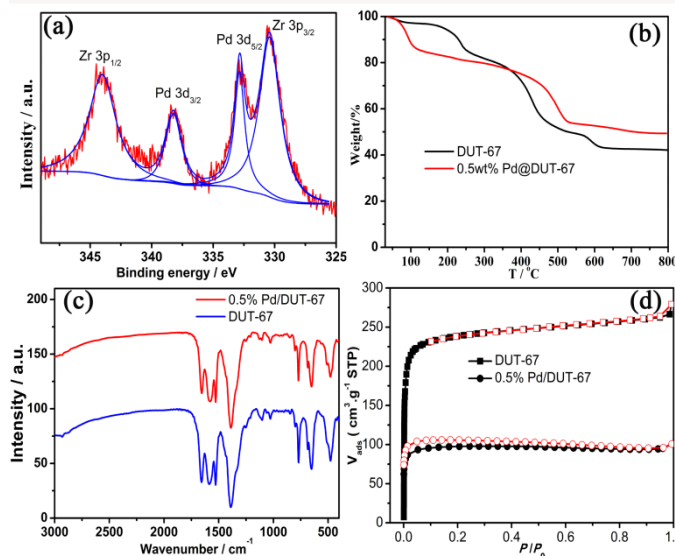


Fig.3.(a) XPS curve of 0.5% Pd/DUT; (b) TG curve of DUT and 0.5% Pd/DUT; (c) IR curve of DUT and 0.5% Pd/DUT and (d) Nitrogen adsorption isotherms of DUT and 0.5% Pd/DUT at 77K.

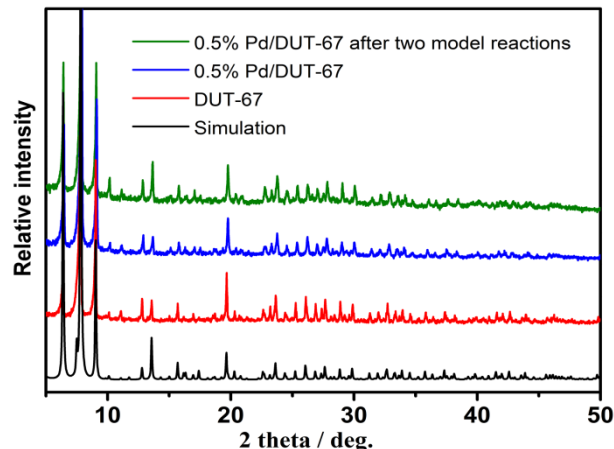
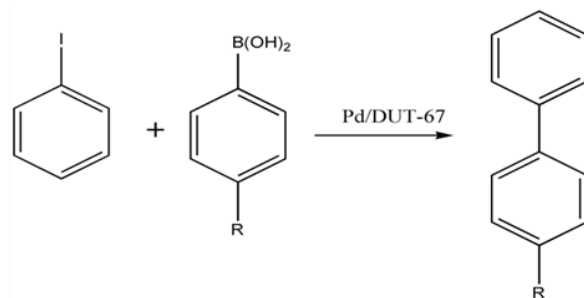


Fig. 4 PXRD curve of theoretical DUT-67, experimental DUT-67, 0.5% Pd/DUT-67 before and after catalytic reaction.

fact that Pd NPs covered on the holes or inset in the cavity. As shown in Fig. 4. PXRD patterns of the as-synthesized DUT-67 and 0.5% Pd/DUT-67 are well agreement with the simulated pattern of DUT-67, indicating the whole framework keep stable after the loading of Pd NPs. Meanwhile, no apparent peaks of Pd NPs can be found, which can be attributed to short orderliness of Pd NPs.

Catalytic property in Suzuki coupling reaction



Scheme 1. Sketch of Suzuki coupling reaction.

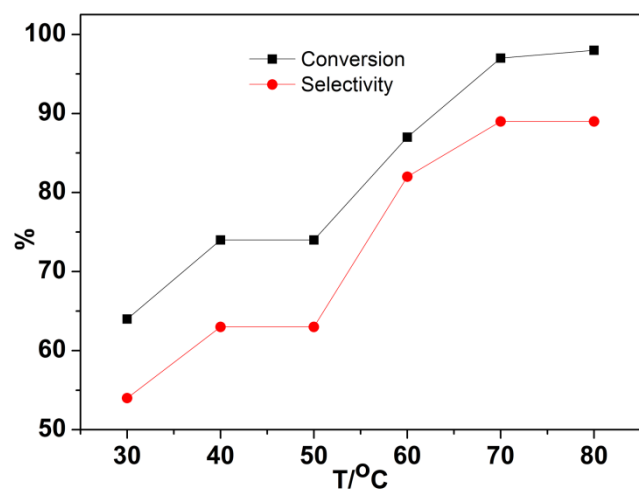


Fig. 5 the relation of conversion or selectivity vs temperature under the medium of water-ethanol mixed solvent and the base of K_2CO_3 .

Table 1. Effect of solvent and base for Suzuki-coupling reaction of iodobenzene and phenylboronic acid using 0.5% Pd/DUT-67 as catalyst at 70 °C.

Exp. ID	Solvent	Base	Conversion (%)	Selectivity (%)
1	water+ethanol	triethylamine	98	34.2
2	water+ethanol	triethanolamine	77.4	21.0
3	water+ethanol	CeF	37.7	0
5	water+ethanol	K_2CO_3	99.0	89.0
6	DMF	K_2CO_3	0	0
7	water	K_2CO_3	99.0	27.0
8	ethanol	K_2CO_3	98.0	84.0

As Suzuki coupling reaction is a classical model reaction with Pd catalysis in the base condition (scheme 1), we carried out a series of reaction between iodobenzene and phenylboronic acid to identify the catalytic performance of Pd/DUT-67. Firstly, the best conditions of catalytic reaction, consisting of temperature, solvent and base, were identified. Reaction temperature is an important factor. By changing the temperature from 30 to 80 °C at 10°C intervals under the medium of water-ethanol mixed solvent and the base of K_2CO_3 , the effects of temperature on conversion and selectivity were obtained, as shown in Fig. 5. It is found that 70 °C is the most suitable temperature. Solvent is also critical for Suzuki coupling reaction. The effect of reaction solvent often plays an important role. It involves a series of identification from the mixture solvent of ethanol- water to pure water and DMF under a certain base of K_2CO_3 . As can be seen from the table 1, in the solvent of water, the selectivity (27.33%) is very low in spite of having high conversion of 99%. For the case of ethanol solvent, comparing the pure water to the mixture solvent, it is observed that although the conversion kept high, the yield of the product was decreased rapidly. However, both conversion and selectivity of catalytic reaction are zero in the solvent of DMF. Therefore, it is found that the mixed solvent of water-ethanol is the most appropriate solvent. Meanwhile, base is also critical factor in Suzuki- coupling reaction. In this regard, different kinds of base, consisting of inorganic base (K_2CO_3 , CsF) and organic base (triethylamine, triethanolamine), had been examined. Organic bases exhibit low selectivity regardless

of high conversion. Among two kinds of inorganic bases, CsF has low conversion and low selectivity, while K_2CO_3 indicates high conversion and selectivity. Generally, K_2CO_3 is the best base in this catalytic reaction.

Secondly, the effect of loading value of Pd on catalytic performance was studied. As the loading value of Pd increases to 1%, the conversion keeps unchangeable, while the selectivity gradually decreases. This may be due to the fact that the Pd NPs have integrates (see Fig. S1). As the loading value of Pd decreases to 0.3%, both conversion and selectivity reduced to 93.2% and 14.3%, owing to the fact that the amount of catalyst is insufficient for whole reaction. Therefore, the 0.5% Pd is optimal loading value. For the case of 0.5%Pd/DUT-67, the influence of substituent group in phenylboronic acid was further examined. If replacing 4-chlorophenylboronic acid with phenylboronic acid, the conversion is up to 98% and the selectivity has reduced to 76%. When p-tolylboronic acid is substituted for phenylboronic acid, the conversion is still unchangeable and the selectivity has reduces a little and reached to 81.8%. It is found that Pd/DUT-67 prefers to phenylboronic acid with electron donating groups. Moreover, a series of blank experiments were also compared. After catalytic reaction, the PXRD curve indicates that the whole framework keep stable, as shown in Fig. 4. And SEM image (see Fig. S4b) also confirms this point. Therefore, it is observed that 0.5%Pd/DUT-67 is good catalyst of suzuki coupling reaction. Reusable experiments shows at the 4th cycle the conversion still keeps at c. a. 80%, as shown in Fig. S5-6.

Table 2 effect of catalyst on Suzuki coupling reaction at 70 °C , water-ethanol mixed solvent and K_2CO_3 .

ID	R	Catalyst	Conversion (%)	Selectivity (%)
1	H	1.0%Pd@DUT-67	99.0	78.9
2	H	0.3%Pd@DUT-67	93.2	14.3
3	H	0.5%Pd@DUT-67	99.0	89.0
4	CH ₃	0.5%Pd@DUT-67	98.0	81.8
5	Cl	0.5%Pd@DUT-67	98.0	76.0
6	H	DUT	48.8	0
7	H	No K_2CO_3	30.0	42.0
8	H	No catalyst	64.7	0

Owing to huge application of aniline in the industry of colourant, resin and medicine, nitrobenzene hydrogenation is an important catalytic model reaction. In this study, hydrogenation of nitrobenzene under relatively mild conditions was used to evaluate the catalytic performance of Pd/DUT-67. Firstly, we conducted blank experiment. If this reaction was carried out without catalyst, there was no aniline in the product. Then, we investigated the effect of reaction temperature on the catalytic performance. Table 4 illustrates the conversion and selectivity as a function of temperature. At 30 °C, the conversion is only 42%, while the selectivity has reached 99%. As the temperature increases, the conversion gradually enhances and reaches the maximum of 99% at 60 °C. If using 1.0%Pd/DUT-67 instead of 0.5%Pd/DUT-67, they feature same catalytic performance at 60 °C, as shown in Table 3. After catalytic experiment, the PXRD pattern exhibits the whole frameworks keep stable, as shown in Fig. 4. However, when the loading value of Pd reduces to 0.3%,

the conversion is very low. Thus, 0.5% Pd is the most suitable loading value.

Table 3. Effect of temperature for Nitrobenzene hydrogenation

ID	T/°C	Catalyst	Conversion (%)	Selectivity (%)
1	60	DUT	0	0
2	60	No catalysis	0	0
3	30	0.5% Pd/DUT-67	42.0	99.0
4	40	0.5% Pd/DUT-67	85.1	99.0
5	50	0.5% Pd/DUT-67	92.4	99.0
6	60	0.5% Pd/DUT-67	99.0	99.0
7	60	1.0% Pd/DUT-67	99.0	99.0
8	60	0.3% Pd/DUT-67	10.8	99.0

Conclusions

In summary, we have prepared three different loading Pd NPs supported micro-crystal DUT-67 MOF. Via various characteristics, it is observed that Pd NPs well distributed in the interface of DUT-67 with the diameter of 3.5 nm. Catalytic measurements indicate that they have good catalytic performance in the Suzuki coupling reaction, where the best catalytic condition is ethanol-water mixed solvent as media, K_2CO_3 as base and at 70 °C. Furthermore, after previous reaction, nitrobenzene hydrogenation model reaction was examined. It is found that when the temperature is up to 60 °C, both conversion and selectivity have reached 99%. Therefore, it is observed that Pd NPs/DUT-67 shows high catalytic performance.

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Notes and references

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- (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472; (b) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213-1214.
- (a) Y. Basdogan and S. Keskin, *CrystEngComm*, 2015, **17**, 261-275; (b) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Ferey, *Angew. Chem. Int. Ed.*, 2008, **47**, 4144-4148; (c) N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933-969; (d) Y. L. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, *Angew. Chem. Int. Ed.*, 2007, **46**, 3278-3283; (e)
- (a) E. Haldoupis, S. Nair and D. S. Sholl, *J. Am. Chem. Soc.*, 2012, **134**, 4313-4323; (b) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*,

- 2012, **112**, 869-932; (c) N. Nijem, H. H. Wu, P. Canepa, A. Marti, K. J. Balkus, T. Thonhauser, J. Li and Y. J. Chabal, *J. Am. Chem. Soc.*, 2012, **134**, 15201-15204; (d) M.-H. Zeng, Z. Yin, Y.-X. Tan, W.-X. Zhang, Y.-P. He and M. Kurmoo, *J. Am. Chem. Soc.*, 2014, **136**, 4680-4688; (e) C. Zlotea, D. Phanon, M. Mazaj, D. Heurtaux, V. Guillerme, C. Serre, P. Horcajada, T. Devic, E. Magnier, F. Cuevas, G. Ferey, P. L. Llewellyn and M. Latroche, *Dalton Trans.*, 2011, **40**, 4879-4881; (f) L. Xie, D. Liu, H. Huang, Q. Yang, C. Zhong, *Chem. Eng. J.* 2014, **246**, 142-149; (g) M. Tong, Q. Yang, Y. Xiao, C. Zhong, *Phys. Chem. Chem. Phys.* 2014, **16**, 15189-15198.
- (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459; (b) B. Y. Li, Y. M. Zhang, D. X. Ma, L. Li, G. H. Li, G. D. Li, Z. Shi and S. H. Feng, *Chem. Commun.*, 2012, **48**, 6151-6153; (c) S. Ou and C.-D. Wu, *Inorganic Chemistry Frontiers*, 2014, **1**, 721-734; (d) F. Xamena, A. Abad, A. Corma and H. Garcia, *J. Catal.*, 2007, **250**, 294-298; (e) F. J. Song, C. Wang, J. M. Falkowski, L. Q. Ma and W. B. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 15390-15398; (f) M. Zhao, S. Ou and C. D. Wu, *Acc. Chem. Res.*, 2014, **47**, 1199-1207.
- (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330-1352; (b) J. Y. An, C. M. Shade, D. A. Chengelis-Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 1220-1223; (c) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Am. Chem. Soc.*, 2007, **129**, 7136-7144; (d) A. D. Burrows, *CrystEngComm*, 2011, **13**, 3623-3642; (e) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun and S. L. Qiu, *Inorg. Chem.*, 2006, **45**, 3582-3587; (f) C. Wang and W. B. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 4232-4235; (g) K. A. White, D. A. Chengelis, K. A. Gogick, J. Stehman, N. L. Rosi and S. Petoud, *J. Am. Chem. Soc.*, 2009, **131**, 18069-+; (h) M. Xue, G. S. Zhu, Y. X. Li, X. J. Zhao, Z. Jin, E. Kang and S. L. Qiu, *Cryst. Growth Des.*, 2008, **8**, 2478-2483.
- (a) J. B. Peng, Q. C. Zhang, X. J. Kong, Y. Z. Zheng, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. P. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314-3317; (b) D. Pinkowicz, R. Podgajny, B. Nowicka, S. Chorazy, M. Reczynski and B. Sieklucka, *Inorganic Chemistry Frontiers*, 2015, **2**, 10-27; (c) C. Z. Ruan, R. Wen, M. X. Liang, X. J. Kong, Y. P. Ren, L. S. Long, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2012, **51**, 7587-7591; (d) M.-H. Zeng, M.-C. Wu, H. Liang, Y.-L. Zhou, X.-M. Chen and S.-W. Ng, *Inorg. Chem.*, 2007, **46**, 7241-7243; (e) Y. Z. Zheng, M. L. Tong, W. X. Zhang and X. M. Chen, *Angew. Chem. Int. Ed.*, 2006, **45**, 6310-6314.
- (a) S. Mendiratta, M. Usman, T. T. Luo, B. C. Chang, S. F. Lee, Y. C. Lin and K. L. Lu, *Cryst. Growth Des.*, 2014, **14**, 1572-1579; (b) T. Tachikawa, J. R. Choi, M. Fujitsuka and T. Majima, *J. Phys. Chem. C*, 2008, **112**, 14090-14101; (c) X.-L. Hu, C.-Y. Sun, C. Qin, X.-L. Wang, H.-N. Wang, E.-L. Zhou, W.-E. Li and Z.-M. Su, *Chem. Commun.*, 2013, **49**, 3564-3566; (d) L. L. Wen, L. Zhou, B. G. Zhang, X. G. Meng, H. Qu and D. F. Li, *J. Mater. Chem.*, 2012, **22**, 22603-22609; (e) Y. Xie, Z. P. Yu, X. Y. Huang, Z. Y. Wang, L. W. Niu, M. Teng and J. Li, *Chemistry-a European Journal*, 2007, **13**, 9399-9405.
- D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem. Int. Ed.*, 2009, **48**, 7502-7513.
- (a) A. Dhakshinamoorthy, M. Opanasenko, J. Cejka and H. Garcia, *Adv. Synth. Catal.*, 2013, **355**, 247-268; (b) M. G. Goesten, J. Juan-Alcaniz, E. V. Ramos-Fernandez, K. Gupta, E. Stavitski, H. van

- Bekkum, J. Gascon and F. Kapteijn, *J. Catal.*, 2011, **281**, 177-187; (c)J. Juan-Alcaniz, J. Ferrando-Soria, I. Luz, P. Serra-Crespo, E. Skupien, V. P. Santos, E. Pardo, F. Xamena, F. Kapteijn and J. Gascon, *J. Catal.*, 2013, **307**, 295-304; (d)L. Mitchell, B. Gonzalez-Santiago, J. P. S. Mowat, M. E. Gunn, P. Williamson, N. Acerbi, M. L. Clarke and P. A. Wright, *Catalysis Science & Technology*, 2013, **3**, 606-617; (e)M. Opanasenko, A. Dhakshinamoorthy, J. Cejka and H. Garcia, *Chemcatchem*, 2013, **5**, 1553-1561; (f)M. Opanasenko, A. Dhakshinamoorthy, Y. K. Hwang, J. S. Chang, H. Garcia and J. Cejka, *ChemSusChem*, 2013, **6**, 865-871; (g)M. Opanasenko, M. Shamzhy and J. Cejka, *Chemcatchem*, 2013, **5**, 1024-1031; (h)K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 6766-6774; (i)P. Valvekens, F. Vermoortele and D. De Vos, *Catalysis Science & Technology*, 2013, **3**, 1435-1445.
10. (a)J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink and F. Kapteijn, *J. Catal.*, 2009, **261**, 75-87; (b)A. M. Rasero-Almansa, A. Corma, M. Iglesias and F. Sanchez, *Chemcatchem*, 2013, **5**, 3092-3100; (c)S. Roy, C. B. George and M. A. Ratner, *J. Phys. Chem. C*, 2012, **116**, 23494-23502.
11. (a)K. S. Jeong, Y. B. Go, S. M. Shin, S. J. Lee, J. Kim, O. M. Yaghi and N. Jeong, *Chemical Science*, 2011, **2**, 877-882; (b)Y. Liu, W. M. Xuan and Y. Cui, *Adv. Mater.*, 2010, **22**, 4112-4135; (c)L. Q. Ma, C. Abney and W. B. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248-1256; (d)G. Q. Kong, S. Ou, C. Zou and C. D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 19851-19857; (e)Y. Liu, X. B. Xi, C. C. Ye, T. F. Gong, Z. W. Yang and Y. Cui, *Angew. Chem. Int. Ed.*, 2014, **53**, 13821-13825; (f)W. M. Xuan, C. C. Ye, M. N. Zhang, Z. J. Chen and Y. Cui, *Chemical Science*, 2013, **4**, 3154-3159.
12. L. B. Vilhelmsen, K. S. Walton and D. S. Sholl, *J. Am. Chem. Soc.*, 2012, **134**, 12807-12816.
13. S. Hermes, M. K. Schroter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2005, **44**, 6237-6241.
14. (a)D. R. Sun, W. J. Liu, Y. H. Fu, Z. X. Fang, F. X. Sun, X. Z. Fu, Y. F. Zhang and Z. H. Li, *Chemistry-a European Journal*, 2014, **20**, 4780-4788; (b)M. Yadav and Q. Xu, *Chem. Commun.*, 2013, **49**, 3327-3329; (c)M. Martis, K. Mori, K. Fujiwara, W. S. Ahn and H. Yamashita, *J. Phys. Chem. C*, 2013, **117**, 22805-22810; (d)A. Aijaz and Q. Xu, *Journal of Physical Chemistry Letters*, 2014, **5**, 1400-1411; (e)A. Aijaz, T. Akita, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 16356-16359; (f)A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Ronnebro, T. Autrey, H. Shioyama and Q. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 13926-13929; (g)H. L. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 11302-+; (h)G. Q. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Toh, S. Matsumura and H. Kitagawa, *Nat. Mater.*, 2014, **13**, 802-806; (i)C. Wang, K. E. deKrafft and W. B. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 7211-7214.
15. (a)T. T. Dang, Y. H. Zhu, J. S. Y. Ngiam, S. C. Ghosh, A. Q. Chen and A. M. Seayad, *ACS Catal.*, 2013, **3**, 1406-1410; (b)M. Yurderi, A. Bulut, M. Zahmakiran, M. Gulcan and S. Ozkar, *Applied Catalysis B-Environmental*, 2014, **160**, 534-541; (c)Y. A. Zhao, M. M. Liu, B. B. Fan, Y. F. Chen, W. M. Lv, N. Y. Lu and R. F. Li, *Catal. Commun.*, 2014, **57**, 119-123; (d)M. M. Zhang, Y. B. Yang, C. Li, Q. Liu, C. T. Williams and C. H. Liang, *Catalysis Science & Technology*, 2014, **4**, 329-332; (e)B. Q. Xia, N. Cao, H. M. Dai, J. Su, X. J. Wu, W. Luo and G. Z. Cheng, *Chemcatchem*, 2014, **6**, 2549-2552; (f)P. Z. Li, K. Aranishi and Q. Xu, *Chem. Commun.*, 2012, **48**, 3173-3175; (g)H. L. Fan, Y. Y. Yang, J. L. Song, G. D. Ding, C. Y. Wu, G. Y. Yang and B. X. Han, *Green Chem.*, 2014, **16**, 600-604; (h)T. Zhang, B. Li, X. F. Zhang, J. S. Qiu, W. Han and K. L. Yeung, *Microporous Mesoporous Mater.*, 2014, **197**, 324-330.
16. (a)Y. Y. Pan, B. Z. Yuan, Y. W. Li and D. H. He, *Chem. Commun.*, 2010, **46**, 2280-2282; (b)F. Wu, L. G. Qiu, F. Ke and X. Jiang, *Inorg. Chem. Commun.*, 2013, **32**, 5-8; (c)H. Khajavi, H. A. Stil, H. Kuipers, J. Gascon and F. Kapteijn, *ACS Catal.*, 2013, **3**, 2617-2626; (d)H. Li, Z. H. Zhu, F. Zhang, S. H. Xie, H. X. Li, P. Li and X. G. Zhou, *ACS Catal.*, 2011, **1**, 1604-1612; (e)J. Hermansdorfer, M. Friedrich, N. Miyajima, R. Q. Albuquerque, S. Kummel and R. Kempe, *Angew. Chem. Int. Ed.*, 2012, **51**, 11473-11477; (f)D. M. Zhang, Y. J. Guan, E. J. M. Hensen, L. Chen and Y. M. Wang, *Catal. Commun.*, 2013, **41**, 47-51.
17. Z.-Y. Gu, J. Park, A. Raiff, Z. Wei and H.-C. Zhou, *ChemCatChem*, 2014, **6**, 67-75.
18. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
19. V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 1231-1237.