ChemPubSoc Europe

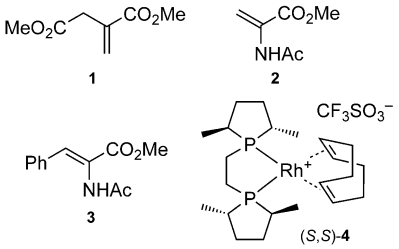
DOI: 10.1002/cctc.201500907

CHEMCATCHEM Communications

Enantioselective Hydrogenation of Olefins Enhanced by Metal–Organic Framework Additives

Beáta Vilhanová,[a, c] Marco Ranocchiari,*[b] and Jeroen A. van Bokhoven*[a, b]

The use of nonprotic solvents (e.g., dichloromethane, toluene) increases the enantioselectivity of the asymmetric hydrogenation of olefins with chiral [Rh(Me-BPE)(cod)]OTf [Me-BPE = 1,2-bis(2,5-dimethylphospholano)ethane; cod = 1,5-cyclooctadiene; OTf = triflate]. Readily available achiral metal–organic frameworks (MOFs) as additives yielded substantially enhanced reactivity. In toluene (but not dichloromethane), the MOFs adsorbed the homogeneous catalyst, which directly reduced rhodium contamination in the products of the reaction. The in situ formed heterogeneous catalyst was reused without loss in selectivity.



Scheme 1. Substrates **1**–**3** and homogeneous catalyst **4** used for asymmetric hydrogenation.

Asymmetric hydrogenation, one of the most common routes towards enantiomerically enriched products, is pivotal in modern synthetic chemistry and in the fine-chemicals industry.[1] Rh^{I} catalysts that have the general formula $[Rh(PP^*)L_2]X$ {PP* = chiral diphosphane; L = olefin, methanol, or other solvent; X = OTf^-, BF_4^-, [3,5-bis(trifluoromethyl)phenyl]borate (BArF), and others} belong to the most popular catalyst classes.[2] For commonly studied substrates (Scheme 1) such as dimethyl itaconate (**1**), methyl 2-acetamidoacrylate (**2**), and methyl (*Z*)-α-acetamidocinnamate (**3**), a variety of ligands [e.g., DIPAMP,[3a] Josiphos,[3b] R-DuPHOS[3c–e] (R = Me, Et, *i*Pr)] yield high enantioselectivity at very low catalyst loadings. Other ligands, such as 1,2-bis(2,5-dimethylphospholano)ethane (Me-BPE), give enantioselectivities that are high but still not comparable with those obtained with the ligands above. The hydrogenation of olefins **1**–**3** by using [Rh(Me-BPE)(cod)]OTf (**4**, cod = 1,5-cyclooctadiene; OTf = triflate) as the catalyst was originally reported with methanol as the solvent. Substrate **1** was hydrogenated with full conversion and up to 91% enantiomeric excess (*ee*) at a catalyst loading of 0.02 mol%.[3f] Similarly, with a catalyst loading of 0.1 mol%, olefins **2** and **3** reacted to give the products with 91.4 and 85% *ee*, respectively.[3c] To the best of our knowledge, examples of **4** as a catalyst for the hydrogenation of **1**, **2**, or **3** in aprotic solvents are not known. However, positive solvent effects have been reported for the Rh(PP*)-catalyzed asymmetric hydrogenation of **1** with an increase in enantioselectivity from 60% *ee* in methanol up to 98% *ee* in dichloromethane.[4] In this publication, we demonstrate the influence of metal-organic frameworks (MOFs) as additives to the reaction mixture.

MOFs are now well established in the area of gas storage and separation[5] and are becoming increasingly popular in catalysis owing to properties such as structural flexibility, high surface area, tunable pore size, and stability.[6] Asymmetric catalysis with the use of MOFs has been described with homochiral frameworks,[7] the synthesis of which requires expensive enantiomerically pure organic precursors prepared in multistep procedures. There are several asymmetric catalysts based on homochiral MOFs,[8] but their expensive synthesis combined with their catalytic performance, which is often lower than that obtained with analogous homogeneous catalysts, have hampered their practical use. Alternatively, an achiral MOF can be functionalized with a chiral molecule,[9] which is a modular and cost-efficient solution also employed in this work. Given that MOFs feature a high surface area and big pores, they can be used as additives in catalysis to adsorb big molecules.[10] For instance, this has been shown in a homogeneous esterification reaction catalyzed by the heteropolyacid $H_3PW_{12}O_{40}$ (HPW) with the $Cu_3(btc)_2$ (HKUST-1; btc = benzene-1,3,5-tricarboxylate) MOF as an adsorbent. The heterogeneous catalyst HPW@HKUST-1 obtained by precipitation was reused at approximately 50% conversion over four runs.[10a] We explored this principle for asymmetric hydrogenation with Rh^{I} catalysts.

In the process of designing our strategy, it was necessary to choose MOFs with appropriate properties. We envisaged that the use of such materials in asymmetric hydrogenation with catalyst **4** required them to have the following features: one,

[a] *B. Vilhanová, Prof. J. A. van Bokhoven*
Department of Chemistry and Applied Biosciences,
Institute for Chemical and Bioengineering, ETH Zürich
Vladimir-Prelog-Weg 1
CH-8093 Zürich (Switzerland)
E-mail: jeroen.vanbokhoven@chem.ethz.ch

[b] *Dr. M. Ranocchiari, Prof. J. A. van Bokhoven*
Laboratory for Catalysis and Sustainable Chemistry
Paul Scherrer Institute (PSI)
CH-5232 Villigen (Switzerland)
E-mail: marco.ranocchiari@psi.ch

[c] *B. Vilhanová*
Department of Organic Technology
University of Chemistry and Technology Prague
Technická 5
CZ-166 28 Prague 6 (Czech Republic)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500907.

a high surface area and pore size to accommodate the metal complex; two, large pore opening and open space to guarantee easy diffusion and to avoid pore blockage; three, mildly coordinating functional groups increasing metal–support interaction but at the same time prevent poisoning of the catalyst. Amino MOFs such as IRMOF-3,[11a] MIXMOF-5-NH_2,[11b] and UMCM-1-NH_2[11c] are good candidates for the purpose. For comparative purposes, standard UMCM-1[11d] was included as well. Such MOFs suffer from decomposition in protic solvents such as methanol[12] but are compatible with aprotic solvents that were chosen for this study.

We started our investigation with itaconate **1** as the substrate and toluene as the solvent in the homogeneous phase. Under unoptimized conditions, (*S*,*S*)-**4** (3.3 mol%) performed the hydrogenation of **1** with 98% conversion and 82% *ee* after a reaction time of 24 h (Table 1, entry 1). Upon repeating the reactions with MOFs added to the mixture (Table 1, entries 2–5), we observed an increase in the *ee* by 4–13%, depending on the material. The highest *ee* was obtained with UMCM-1-NH_2 (Table 1, entry 5), which outperformed the previously reported hydrogenation in methanol (Table 1, entry 6).[3f]

Table 1. Preliminary attempts in the asymmetric hydrogenation of olefin **1** catalyzed by (*S*,*S*)-**4** with MOFs in toluene.[a]

Entry	MOF	Conversion [%]	*ee* [%]
1	none	98	82
2	IRMOF-3	>99	92
3	MIXMOF-5-NH_2	98	86
4	UMCM-1	96	89
5	UMCM-1-NH_2	>99	95
6[b]	none	>99	91

[a] Reaction conditions: c(**1**) = 0.19 M, n(**1**) = 0.106 mmol, RT, 24 h, $p(H_2)$ = 0.3 MPa, 3.3 mol% catalyst loading, m(MOF) = 9 mg. [b] c(**1**) = 2.5 M, 28 °C, 30 min, $p(H_2)$ = 1.0 MPa, 0.02 mol% catalyst loading, [Rh(Me-BPE)(cod)]BF_4 used as catalyst and methanol as solvent.[3f]

This showed a significant enhancement in the catalytic performance with MOFs as additives. We constantly observed that the MOFs adsorbed the Rh complex—the solution, orange in the beginning of the experiment, turned virtually colorless during the reaction. Simultaneously, the MOFs changed color to orange-red, typical of a Rh catalyst, and maintained its crystallinity, as evident by the images collected by a microscope with polarized light (Figure 1).

We therefore performed the asymmetric hydrogenation of olefins **1** and **2** with all four MOFs with a reaction time of 24 h. The aim was to quantify the amount of rhodium adsorbed. Quantitative inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Table 2) indicated that the MOFs adsorbed 75–94% of the Rh catalyst, depending on the nature of the MOF. The MOF with the highest porosity (i.e., UMCM-1-NH_2) adsorbed approximately 92% of the catalyst. Less porous MOFs such as IRMOF-3 and MIXMOF-5-NH_2 adsorbed approximately 5–10% less than that with the UMCM-1 topology. IRMOF-3, which is the fully functionalized NH_2-MOF, adsorbed less than MIXMOF-5-NH_2, probably because of the overcrowded presence of Rh on the external surface of the crystals.[13] Unfunctionalized UMCM-1 adsorbed the same amount of Rh in the hydrogenation of **2** as its amino analogue, whereas it captured 87% in the hydrogenation of **1**. Interestingly, the amino functional group played a minimal role in the adsorption of the catalyst within the pores. Figure 2 depicts the catalyst with a size of approximately 10 Å adsorbed within the cages of the materials. In the cases of IRMOF-3 and MIXMOF-5-NH_2, the cat-

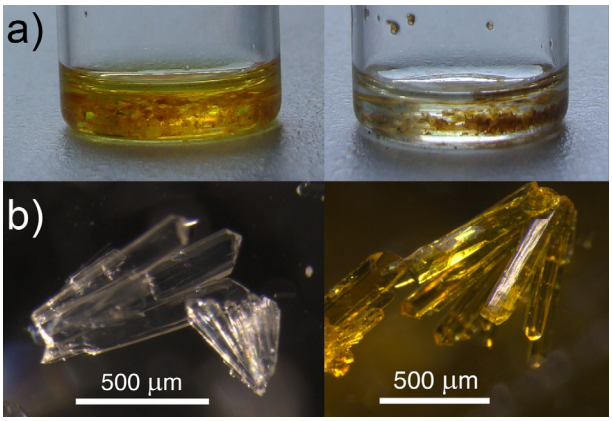


Figure 1. a) Reaction mixture before (left) and after (right) asymmetric hydrogenation of **1** by employing UMCM-1-NH_2. b) Unmodified UMCM-1-NH_2 (left) and UMCM-1-NH_2 containing catalyst **4** adsorbed from the reaction mixture (right).

Table 2. Amount of adsorbed complex (*S*,*S*)-**4** by the MOFs during asymmetric hydrogenation of olefin **1** and **2** in toluene.[a]

Entry	Substrate	MOF	Rh adsorbed [%][b]
1	**1**	IRMOF-3	75
2	**1**	MIXMOF-5-NH_2	82
3	**1**	UMCM-1-NH_2	92
4	**1**	UMCM-1	87
5	**2**	IRMOF-3	88
6	**2**	MIXMOF-5-NH_2	89
7	**2**	UMCM-1-NH_2	94
8	**2**	UMCM-1	93

[a] Reaction conditions: c(**1**) = 0.19 M, c(**2**) = 0.20 M, n(olefin) = 0.323 mmol, RT, 24 h, $p(H_2)$ = 0.3 MPa, 1 mol% catalyst loading, m(MOF) = 14 mg. [b] Calculated from the Rh content in the reaction mixture as determined by ICP-OES.

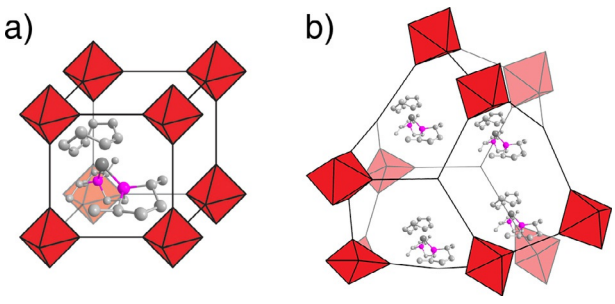


Figure 2. Schematic representation of **4** adsorbed in a) IRMOF-3 or MIXMOF-5-NH_2 and b) UMCM-1 or UMCM-1-NH_2 materials.

alyst has a size similar to the size of the pore opening, which conforms to the lower amounts of **4** adsorbed. UMCM-1 materials feature channels that are >30 Å, which affords extraordinary capacity for adsorption.

The fact that the MOFs adsorb chiral Rh complexes such as **4** allowed the heterogenization of the homogeneous catalyst and consequent recycling. Substrates **1** and **2** were hydrogenated with 1 mol% of (*S*,*S*)-**4** for 16 h in the presence of UMCM-1-NH_2 (Table 3, entries 1 and 3). After the first catalytic run, the MOF containing (*S*,*S*)-**4** was separated from the reaction mixture, washed with toluene, and recycled (Table 3, entries 2 and 4). A general increase in enantioselectivity was observed in the second catalytic run; however, a decrease in catalytic activity was evident. The higher activity in the first run reflects the contribution of the homogeneously catalyzed hydrogenation, which is eliminated in the second run by washing of the MOF. In addition, the catalyst is highly oxygen sensitive, which can also explain some loss in activity. Thus, this proof-of-concept experiment shows that recycling is possible. A "hot" filtration experiment[14] confirmed that only 1–2% of Rh leached out of the heterogeneous catalyst after the second run and, thus, showed that in the first run the reaction was both homogeneous and heterogeneous and purely heterogeneous in the second. The enhanced selectivity is speculatively attributed to the increased steric hindrance of the active site within the confined space of the pores.

Table 3. Asymmetric hydrogenation of olefins **1** and **2** by using UMCM-NH_2 and (*S*,*S*)-**4** in toluene and repeated usage of the MOF in catalysis.[a]

Entry	Substrate	Run	Conversion [%]	*ee* [%]
1	**1**	1	75	94
2	**1**	2	11	95
3	**2**	1	>99	96
4	**2**	2	56	98

[a] Reaction conditions: c(**1**) = 0.19 M, n(**1**) = 0.106 mmol, RT, 16 h, $p(H_2)$ = 0.3 MPa, 1 mol% catalyst loading, m(MOF) = 14 mg.

Optimization of the reaction conditions for the homogeneous hydrogenation was necessary because of the low activity of the catalyst. This decreased activity in toluene relative to that in methanol might be due to the coordination of toluene to Rh, which causes deactivation of the catalyst.[15] For this reason, we also screened dichloromethane as a solvent. Substrates **1**–**3** were easily hydrogenated in dichloromethane and toluene with (*S*,*S*)-**4** as the catalyst to give very good selectivity by using a 3-addition protocol (3AP). Thus, under optimized conditions, the reaction was started with 1 mol% of (*S*,*S*)-**4** under 0.3 MPa of H_2. After a reaction time of 4 h, one additional equivalent of substrate was added, which thereby reduced the catalyst loading to 0.5 mol%. Another equivalent of substrate was added after 4 h, which further reduced the amount of the catalyst to 0.33 mol%. Afterwards, the reaction was left at room temperature under 0.3 MPa of H_2 for 14 h. In toluene, the MOF adsorbed the complex almost quantitatively (Table 2) and yielded similar catalytic results to those observed above. On the other hand, in dichloromethane a significant amount of the Rh catalyst still remained in the solvent at the end of the reaction.

Dimethyl itaconate (**1**) was hydrogenated in dichloromethane with excellent conversion and high selectivity (up to 92% *ee*), and the addition of the MOFs did not lead to any significant differences (Table 4, entries 1–5). Given that we observed that the MOF did not fully adsorb the catalyst in dichloromethane, the reaction was mainly homogeneous and the MOF additive had no significant effect. In toluene, the 3AP for the hydrogenation of **1** generally gave a rather low conversion (Table 4, entry 6), lower than the initial protocol (Table 1), which was done at a higher catalyst loading. With the addition of MOFs (Table 4, entries 7–10), the conversion increased. Most notably, UMCM-1 furnished an almost threefold enhancement (Table 4, entry 10). Maximum enantioselectivity was observed upon using UMCM-1-NH_2 as the additive (Table 4, entry 9). We again note that the enantioselectivities obtained in dichloromethane and toluene were equal or higher than those reported in the literature with methanol as the solvent with the same catalyst (Table 1, entry 6).[3f]

Table 4. Asymmetric hydrogenation of olefins **1**–**3** catalyzed by (*S*,*S*)-**4** with the 3AP.[a]

Entry	MOF	Solvent	Substrate					
			1		**2**		**3**	
			Conversion [%]	*ee* [%]	Conversion [%]	*ee* [%]	Conversion [%]	*ee* [%]
1	none	CH_2Cl_2	>99	92	>99	94	92	94
2	IRMOF-3	CH_2Cl_2	>99	92	>99	94	99	94
3	MIXMOF-5-NH_2	CH_2Cl_2	>99	92	>99	94	62	94
4	UMCM-1-NH_2	CH_2Cl_2	>99	92	>99	94	90	94
5	UMCM-1	CH_2Cl_2	>99	92	>99	94	81	94
6	none	toluene	10	92	30	98	43	98
7	IRMOF-3	toluene	10	90	49	97	51	99
8	MIXMOF-5-NH_2	toluene	12	92	54	97	73	99
9	UMCM-1-NH_2	toluene	21	94	51	97	48	99
10	UMCM-1	toluene	27	91	64	98	55	97

[a] Reaction conditions: Initial substrate concentrations c(**1**) = 0.19 M, c(**2**) = 0.20 M, c(**3**) = 0.13 M, initial substrate amount n = 0.323 mmol, RT, 3AP (4 + 4 + 14 h), $p(H_2)$ = 0.3 MPa, catalyst loading 1–0.5–0.33 mol%, m(MOF) = 14 mg.

Hydrogenation of methyl acrylate **2** by using the 3AP in dichloromethane afforded the product with >99% conversion and 94% *ee* with and without the addition of MOFs (Table 4, entries 1–5). Again, we attribute this to the fact that the catalyst is not adsorbed in the MOFs. The homogeneous reaction in toluene gave 98% *ee* with 30% conversion (Table 4, entry 6), and the addition of the MOFs generally increased the conversion by up to a factor of two (Table 4, entries 7–10), with a maximum value of 64% achieved with UMCM-1 (Table 4, entry 10).

Hydrogenation of methyl 2-acetamidocinnamate (**3**) by using the 3AP did not proceed as fast as in the case of substrates **1** and **2**. In dichloromethane, the homogeneous attempt yielded the product with 92% conversion and 94% *ee* (Table 4, entry 1). The addition of IRMOF-3 increased the reactivity of the catalytic system, which led to full conversion (Table 4, entry 2), whereas other MOFs displayed a decrease in catalytic activity (Table 4, entries 3–5). However, consistent improvements were shown if toluene was used as the solvent. The homogeneous hydrogenation of **3** resulted in 43% conversion and 98% *ee* (Table 4, entry 6). The addition of MOFs improved the conversion (Table 4, entries 7–10) up to 73% with MIXMOF-5-NH_2 (Table 4, entry 8). The enantioselectivity remained between 97 and 99% *ee*, close to that of the homogeneous attempt (Table 4, entry 6). The obtained enantioselectivities were much higher than the published value with the same catalyst in methanol (85% *ee*).[3c]

The enhanced conversion in catalytic attempts with MOF additives might be due to the enhanced stability of the molecular catalyst inside the cage of the MOF and local concentration effects. We speculate that, owing to the confined space within the MOF, the formation of inactive dimers or Rh–arene complexes[16] might be prevented during hydrogenation. In this way, higher catalytic activity is reached, similarly to that observed in nanoreactors,[17] but still lower than that observed in protic and/or oxygenated solvents.[3c,f]

In summary, the enantioselectivity of the asymmetric hydrogenation of olefins **1**–**3** with (*S*,*S*)-**4** as a catalyst was increased by using aprotic solvents such as dichloromethane and toluene instead of protic solvents such as methanol. Furthermore, a significant increase in conversion was achieved in toluene with known (thus readily available) achiral metal–organic frameworks (MOFs) as additives, which adsorbed up to 96% of the catalytic complex from the reaction mixture. This enabled recycling of the catalyst while retaining enantioselectivity and conveniently reduced the contamination of the product by rhodium. This study opens new perspectives in the use of achiral MOFs functionalized with enantiopure complexes as heterogeneous catalysts for asymmetric hydrogenation and adds a conceptually new tool to improve the performance of homogeneous catalysts, constituting a stand-alone category beside homochiral MOFs, which are costly and not as tunable as the system stemming from highly versatile homogeneous catalysts.

Acknowledgements

Financial support from the Sciex Programme (Grant No. 13.274) is acknowledged.

Keywords: alkenes · asymmetric catalysis · hydrogenation · metal–organic frameworks · rhodium

[1] a) N. B. Johnson, I. C. Lennon, P. H. Moran, J. A. Ramsden, *Acc. Chem. Res.* **2007**, *40*, 1291–1299; b) H. Shimizu, I. Nagasaki, K. Matsumura, N. Sayo, T. Saito, *Acc. Chem. Res.* **2007**, *40*, 1385–1393; c) M. E. Fox, M. Jackson, G. Meek, M. Willets, *Org. Process Res. Dev.* **2011**, *15*, 1163–1171; d) D. J. Ager, A. H. M. de Vries, J. G. de Vries, *Chem. Soc. Rev.* **2012**, *41*, 3340–3380.

[2] a) W. Zhang, Y. Chi, X. Zhang, *Acc. Chem. Res.* **2007**, *40*, 1278–1290; b) S. Lühr, J. Holz, A. Börner, *ChemCatChem* **2011**, *3*, 1708–1730.

[3] a) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946–5952; b) A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066; c) M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518–8519; d) M. J. Burk, M. F. Gross, T. G. P. Harper, C. S. Kalberg, J. R. Lee, J. P. Martinez, *Pure Appl. Chem.* **1996**, *68*, 37–44; e) M. J. Burk, G. Casy, N. B. Johnson, *J. Org. Chem.* **1998**, *63*, 6084–6085; f) C. J. Pilkington, A. Zanotti-Gerosa, *Org. Lett.* **2003**, *5*, 1273–1275.

[4] B. Schäffner, V. Andrushko, J. Bayardon, J. Holz, A. Börner, *Chirality* **2009**, *21*, 857–861.

[5] a) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477–1504; b) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294–1314; c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781.

[6] a) M. Ranocchiari, J. A. van Bokhoven, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6388–6396; b) J. Gascon, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, *ACS Catal.* **2014**, *4*, 361–378; c) R. E. Morris, J. Čejka, *Nat. Chem.* **2015**, *7*, 381–388; d) Z. Fang, B. Bueken, D. E. De Vos, R. A. Fischer, *Angew. Chem. Int. Ed.* **2015**, *54*, 7234–7254; *Angew. Chem.* **2015**, *127*, 7340–7362.

[7] a) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1256; b) Y. Liu, W. Xuan, Y. Cui, *Adv. Mater.* **2010**, *22*, 4112–4135; c) R. E. Morris, X. Bu, *Nat. Chem.* **2010**, *2*, 353–361; d) C. Wang, M. Zheng, W. Lin, *J. Phys. Chem. Lett.* **2011**, *2*, 1701–1709; e) G. Nickerl, A. Henschel, R. Grünker, K. Gedrich, S. Kaskel, *Chem. Ing. Tech.* **2011**, *83*, 90–103; f) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196–1231; g) J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 5213–5216.

[8] a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; b) C. D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941; c) G. Li, W. Yu, J. Ni, T. Liu, Y. Liu, E. Sheng, Y. Cui, *Angew. Chem. Int. Ed.* **2008**, *47*, 1245–1249; *Angew. Chem.* **2008**, *120*, 1265–1269.

[9] A. L. W. Demuynck, M. G. Goesten, E. V. Ramos-Fernandez, M. Dusselier, J. Vanderleyden, F. Kapteijn, J. Gascon, B. F. Sels, *ChemCatChem* **2014**, *6*, 2211–2214.

[10] a) N. Janssens, L. H. Wee, S. Bajpe, E. Breynaert, C. E. A. Kirschhock, J. A. Martens, *Chem. Sci.* **2012**, *3*, 1847–1850; b) S. Sartipi, M. José Valero Romero, E. Rozhko, Z. Que, H. A. Stil, J. de With, F. Kapteijn, J. Gascon, *ChemCatChem* **2015**, *7*, 3243–3247; Valero Romero, E. Rozhko, Z. Que, H. A. Stil, J. de With, F. Kapteijn, J. Gascon, *ChemCatChem* **2015**, *7*, 3243–3247.

[11] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; b) H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2010**, *327*, 846–850; c) Z. Wang, K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* **2009**, *48*, 296–306; d) K. Koh, A. G. Wong-Foy, A. J. Matzger, *Angew. Chem. Int. Ed.* **2008**, *47*, 677–680; *Angew. Chem.* **2008**, *120*, 689–692.

[12] S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 14176–14177.

[13] M. Ranocchiari, C. Lothschütz, D. Grolimund, J. A. van Bokhoven, *Proc. R. Soc. A* **2012**, *468*, 1985 – 1999.
[14] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485 – 493.
[15] R. Giernoth, P. Huebler, J. Bargon, *Angew. Chem. Int. Ed.* **1998**, *37*, 2473 – 2475; *Angew. Chem.* **1998**, *110*, 2649 – 2651.
[16] D. Heller, A. H. M. de Vries, J. G. de Vries in *The Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2006**, pp. 1483 – 1516.
[17] Q. Yang, D. Han, H. Yang, C. Li, *Chem. Asian J.* **2008**, *3*, 1214 – 1229.

Received: August 14, 2015
Published online on November 4, 2015