# Heterogeneous Catalysis

# Mild and Selective Catalytic Hydrogenation of the C=C Bond in $\alpha,\beta$ -Unsaturated Carbonyl Compounds Using Supported **Palladium Nanoparticles**

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Abstract: Chemoselective reduction of the C=C bond in a variety of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds using supported palladium nanoparticles is reported. Three different heterogeneous catalysts were compared using 1 atm of H<sub>2</sub>: 1) nano-Pd on a metal-organic framework (MOF: Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr)), 2) nano-Pd on a siliceous mesocellular foam (MCF: Pd<sup>0</sup>-AmP-MCF), and 3) commercially available palladium on carbon (Pd/C). Initial studies showed that the

# Introduction

Catalytic hydrogenation reactions have proven to be highly important transformations in organic synthesis. In 2013, one fourth of all drugs, marketed or in clinical trials, involved at least one hydrogenation step in their synthetic route.<sup>[1]</sup> The chemoselective hydrogenation of olefinic bonds in the presence of other reducible functional groups such as aldehydes or ketones is an important but particularly challenging transformation. Most catalysts, especially heterogeneous ones, are severely limited in terms of selectivity and their applicability is restricted to non-challenging substrates.<sup>[2]</sup>

Metal-organic frameworks (MOFs)<sup>[3]</sup> are crystalline porous materials with very high surface areas and tunable pore sizes from micro- to mesopores, that have been successfully applied

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	Supporting information for this article can be found under http://
	dx doi ora/10 1002/chem 201600878

Chem. Eur. J. 2016, 22, 7184 - 7189

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7184

Pd@MOF and Pd@MCF nanocatalysts were superior in activity and selectivity compared to commercial Pd/C. Both Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and Pd<sup>0</sup>-AmP-MCF were capable of delivering the desired products in very short reaction times (10-90 min) with low loadings of Pd (0.5-1 mol%). Additionally, the two catalytic systems exhibited high recyclability and very low levels of metal leaching.

as supports in heterogeneous catalysis.<sup>[4]</sup> On the other hand, porous siliceous materials such as mesocellular foams (MCFs), although amorphous, consist of an adjustable three-dimensional network of pores and display a significantly broader range of pore sizes of up to 50 nm. Therefore they can promote a more efficient mass transfer. The siliceous MCF that has been the subject of work in our group<sup>[5]</sup> delivers a high surface concentration of silanol groups that can be further functionalized. In a similar way, the inner surface of MOFs' pores can be tailored by anchoring functional groups onto the organic linkers, either directly in the synthesis process or through postsynthetic modification techniques. Both MOFs<sup>[6]</sup> and MCFs<sup>[7]</sup> have been successfully used to support metallic nanocatalysts. The confined environment created around the catalyst can lead to a different reactivity than that observed in solution. Often, this reactivity is also dependent on the size and shape of the nanoparticles.<sup>[8]</sup> Furthermore, the porous nature of the supports prevents aggregation of the metal. Finely dispersed nanoparticles with narrow size distributions can easily be obtained and protected in the absence of additional surfactants and their surface-dependent catalytic properties can be preserved.

In this study we have evaluated and compared the efficiency of palladium nanoparticles supported on siliceous mesocellular foam (Pdº-AmP-MCF, 8 wt % Pd)<sup>[9]</sup> and on a metal-organic framework (Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr), 8 wt % Pd)<sup>[4b, 10]</sup> with that of Pd/C. Both porous matrices have been pre-functionalized with pendant -NH<sub>2</sub> groups, in order to stabilize the nanoparticles and to minimize Pd leaching upon repeated uses. Herein, we demonstrate the efficiency of the two porous nanocatalysts in the chemoselective reduction of the olefinic double bond of different  $\alpha_{i}\beta$ -unsaturated carbonyl compounds.



# **Results and Discussion**

The hydrogenation of cinnamaldehyde (1 a) was chosen as the model reaction. The possible pathways the reaction can take are illustrated in Scheme 1. Under ideal conditions, the only operating pathway would be the selective reduction of the C=C double bond (Pathway A), leading to exclusive formation of 3-phenylpropanal (2a). Over-reduction to 3-phenylpropan-1ol (3a; pathways C and C') is favored by longer reaction times and/or harsher reaction conditions, such as higher temperature and increased H<sub>2</sub> pressure. Additionally, the selectivity can be affected by other factors such as the type and morphology of the support, metal dispersion, steric constraints and electronic effects. Literature reports based on Ru and Pt nanoparticles demonstrated that the size of the nanoparticles does play an important role on the selectivity and that larger nanoparticles and aggregates are able to promote selective formation of the allylic alcohol 4a.[11] On these grounds we hypothesized that small, finely dispersed nanoparticles supported on porous MOFs and MCFs would have the right shape, size and environment to favor Pathway A over B and C.



Scheme 1. Possible reaction pathways in the hydrogenation of cinnamaldehyde.

We set out to find the ideal conditions for a selective transformation by evaluating the behavior of the two catalysts (Pd<sup>0</sup>-AmP-MCF and Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr)) together with that of Pd/C in different solvents. As shown in Table 1, the efficiency of Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) was mostly unaffected by the choice of solvent. Overall, excellent conversions (>99%) and relatively high selectivities (89-90%) were obtained within 90 min in all of the solvents examined (Table 1, entries 3-5). Shorter reaction times afforded lower conversions (Table 1, entries 1 and 2). On the contrary, the catalytic performances of Pd<sup>0</sup>-AmP-MCF (Table 1, entries 6-9) and of Pd/C (Table 1, entries 10-13) were dependent on the solvent to a large extent. With Pdº-AmP-MCF, high conversions were obtained in both acetone and EtOAc (88 and 96%, respectively) in only 30 min; however, the selectivity towards the desired 3-phenylpropanal (2a) was higher in the latter solvent (86 vs. 94%; Table 1, entries 6 and 7).<sup>[12]</sup> Interestingly, although full conversion was achieved when the reaction time was prolonged to 60 min in EtOAc, a minor increase in over-reduction of 2a to 3a could be observed (6% vs 8%; Table 1, entry 7 vs. 8). Running the reaction in toluene resulted in lower conversion (66%) and the selectivity decreased to 87% (Table 1, entry 9). For the commercially available Pd/C catalyst, the reaction had in general very poor selectivities (50-73%) and low conversions (36-68%) in all the tested solvents (Table 1, entries 10-13). The reactions catalyzed by Pd/C were generally slower than those catalyzed by the other two nanopalladium catalysts, and among them Pdº-AmP-MCF afforded the highest rates. This may be explained by a facilitated mass transfer of the reagents into the MCF material through the wider pore windows (13 nm for AmP-MCF vs. 1.6 nm for MIL-101-NH<sub>2</sub>(Cr)). It is noteworthy that allylic alcohol 4a could not be observed at any moment in any of the experiments described until this point. To rule out the intermediacy of 4a in the formation of 2a (Pathway D) we attempted the isomerization of the allylic alcohol (4a). However, none of the three catalysts afforded aldehyde 2a. Furthermore, it was demonstrated that 4a is rapidly reduced to 3a (Pathway C') under the reaction conditions (i.e., 1 mol% of Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) under 1 atm H<sub>2</sub> reduces cinnamyl alcohol (4a) into 3-phenylpropan-1-ol (3a) with a TOF three times higher than in the case of cinnamaldehyde). In further control experiments, the attempted hydrogenation of 2a (stirred overnight under 1 atm H<sub>2</sub>) in the presence either Pd<sup>0</sup>-AmP-MCF or Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) did not produce compound 3a. The absence of 3a in these experiments indicates that over-reduction via Pathway C does not occur under the present conditions, and that 3a is only formed from intermediate allylic alcohol 4a, which quickly reduces to form 3a in the reaction mixture (Pathways B+C').

We also considered that the readily oxidizable cinnamaldehyde (**1 a**) could be contaminated with trace amounts of cinnamic acid. This species could then activate the carbonyl moiety towards hydrogenation (via hydrogen bonding), which would favor formation of the over-reduced product **3a** via Pathways B+C'. However, **3a** also was observed in similar amounts when freshly distilled cinnamaldehyde was used.

Table 1. Initial screening of solvents and reaction time for the hydroge- nation of cinnamaldehyde (1 a). <sup>[a]</sup>							
Pd cat. (1 mol%) 1 atm H <sub>2</sub> Solvent (0.4 M) 1a 20 °C, Time 2a				~ <sub>0</sub>	°О ОН За		
Entry	Catalyst	Solvent	t [min]	Conv. [%] <sup>[b]</sup>	2 a/3 a <sup>[b]</sup>	<b>2 a</b> [%] <sup>[b]</sup>	
1	Pd <sup>0</sup> -MIL-101-NH <sub>2</sub> (Cr)	acetone	30	55	85:15	47	
2	_	acetone	60	86	87:13	75	
3		acetone	90	>99	89:11	89	
4		EtOAc	90	>99	90:10	90	
5		toluene	90	>99	89:11	89	
6	Pd <sup>0</sup> -AmP-MCF	acetone	30	88	86:14	76	
7		EtOAc	30	96	94:6	90	
8		EtOAc	60	>99	92:8	92	
9		toluene	30	66	87:13	57	
10	Pd/C <sup>[c]</sup>	acetone	30	40	55:45	22	
11		acetone	60	68	55:45	37	
12		EtOAc	30	50	73:27	37	
13		toluene	30	36	50:50	18	
[a] Unless otherwise noted, reactions were performed on a 0.8 mmol scale under 1 atm of H <sub>2</sub> at 20 °C. [b] Determined by <sup>1</sup> H NMR spectroscopy from the crude reaction mixture. [c] 10 wt% Pd.							

Chem. Eur. J. 2016, 22, 7184 – 7189

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Therefore, the effect of a base additive such as K<sub>2</sub>CO<sub>3</sub>, which could neutralize acidic species in-situ, was investigated for the three different catalysts (Table 2). When Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) was used, the addition of K<sub>2</sub>CO<sub>3</sub> (0.1 equiv) was detrimental for the selectivity (Table 2, entries 1-3 vs. Table 1, entries 3-5). However, these results are consistent with our<sup>[13]</sup> and others'<sup>[14]</sup> recent investigations on the stability of the MIL-101(Cr) framework in basic media. The presence of K<sub>2</sub>CO<sub>3</sub> leads to a degradation of the porous framework, which can no longer prevent the agglomeration of Pd nanoparticles. Large Pd aggregates can then be responsible for the decreased selectivity as discussed above.<sup>[11]</sup> Conversely, for the Pd<sup>0</sup>-AmP-MCF catalyst, which is not base-sensitive, the presence of K<sub>2</sub>CO<sub>3</sub> had a negligible effect on the selectivity in EtOAc (Table 2, entry 4 vs. Table 1, entry 7). However, in acetone the selectivity increased to >99% in the presence of  $K_2CO_3$ , and quantitative formation of 2a was observed within 60 min (Table 2, entries 5 and 6). Compared to the two nanocatalysts, Pd/C still exhibited lower conversions (29-52%) and selectivities (57-82%), even in the presence of base (Table 2, entries 7-10). Other solvents and additives were investigated under similar conditions but this did not lead to any further improvements of the reaction (see the Supporting Information for further details).

Since the addition of base did not improve the selectivity in the reactions catalyzed by Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr), further optimization of this catalytic system was carried out by investigating

<b>Table 2.</b> Influence of base addition and dilution on the Pd-catalyzed hydrogenation reactions. <sup>[a]</sup>						
Pd cat. (1 mol%) 1 atm H <sub>2</sub> $K_2CO_3$ (0.1 equiv) Solvent (0.4 M) 1a 20 °C, Time 2a 3a						
Entry	Catalyst	Solvent	t [min]	Conv. [%] <sup>[b]</sup>	2 a/3 a <sup>[b]</sup>	<b>2 a</b> [%] <sup>[b]</sup>
1	Pd <sup>0</sup> -MIL-101-NH <sub>2</sub> (Cr)	toluene	90	>99	88:12	89
2		acetone	90	>99	69:31	69
3		EtOAc	90	>99	74:26	74
4	Pd⁰-AmP-MCF	EtOAc	30	62	95:5	59
5		acetone	30	67	>99:1	67
6		acetone	60	>99	> <b>99</b> :1	>99
7 <sup>[c]</sup>	Pd/C (10wt%)	toluene	30	38	73:27	28
8 <sup>[c]</sup>		acetone	30	29	62:38	18
9 <sup>[c]</sup>		acetone	60	52	57:43	30
10 <sup>[c]</sup>		EtOAc	30	39	82:18	32
11 <sup>[d]</sup>	Pd <sup>0</sup> -MIL-101-NH <sub>2</sub> (Cr)	toluene	90	>99	95:5	95
12 <sup>[d]</sup>		acetone	30	42	88:12	37
13 <sup>[d]</sup>		acetone	60	72	93:7	67
14 <sup>[d]</sup>		acetone	90	>99	95:5	95
15 <sup>[d]</sup>		EtOAc	90	>99	94:6	94
16 <sup>[d]</sup>		neat	960	25	92:8	23
17 <sup>[d]</sup>	Pd/C <sup>[e]</sup>	acetone	30	37	60:40	22
18 <sup>[d]</sup>		acetone	60	57	60:40	34
19 <sup>[d]</sup>		acetone	90	69	60:40	41
[a] Unless otherwise noted, reactions were performed on a 0.8 mmol scale under 1 atm of $H_2$ at room temperature. [b] Determined by <sup>1</sup> H NMR spectroscopy of the crude reaction mixture. [c] Traces of <b>4a</b> were observed when the performed to string discussion of the crude reaction of the second termined by the second secon						

served when the reaction was allowed to stir, overnight. [d] Reaction diluted from 0.4 to 0.2 M and no base additive used. [e] 10 wt % Pd.

the effect of the substrate concentration. Gratifyingly, we found that lowering the substrate concentration from 0.4 to 0.2 M without the addition of base, improved the selectivity significantly (Table 2, entries 11–15). This surprising effect could be attributed to the presence of Cr Lewis acidic sites in the structure of the MOF, which are prone to be exposed on the surface of the crystals and coordinate to the carbonylic oxygen atoms, activating them towards the undesired reduction of the C=O. Interestingly, in all experiments catalyzed by Pd@MOF, the by-product (3 a) is formed in the earliest stages of the reaction. By diluting the reaction mixture from 0.4 to 0.2 m, the concentration of exposed acidic Cr sites is reduced, decreasing their chances to activate C=O bonds towards undesired reduction. On the other hand, the dilution of the reaction medium could simply render the whole catalyst less active, thus improving the overall selectivity. Changing the solvent still did not drastically affect the outcome of the reactions; quantitative conversions and similarly high selectivities (94-95%) were recorded in each of the three solvents that were examined after 90 min of reaction time. Further diluting the reaction had no beneficial effect and running the reaction under neat conditions afforded a very low conversion with a selectivity of 92% (Table 2, entry 16). For comparison, the use of Pd/C under similar conditions (0.2 m, no base) resulted in lower conversion (69%) and a very poor selectivity (60%) after 90 min (Table 2, entries 17–19). For the reactions with Pd<sup>0</sup>-AmP-MCF, only negligible improvements in selectivity were observed when the reaction was performed without base and with a substrate concentration of 0.2 M compared to the reaction with 0.4 M.

The screening experiments described clearly demonstrate that Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and Pd<sup>0</sup>-AmP-MCF display a significantly higher selectivity for the reduction of the olefinic bond in  $\alpha$ , $\beta$ -unsaturated carbonyl compounds compared to commercially available Pd/C. Even more, the remarkable reactivity of the two nanocatalysts enables them to operate under very mild conditions, avoiding over-reduction of the reaction product. Under the optimized conditions, the well-controlled size and shape of the encapsulated nanoparticles (ca. 2-3 nm; see Supporting Information, Figure S1) in MIL-101-NH<sub>2</sub>(Cr) and in AmP-MCF inhibits the undesired reduction of the C=O bond (Pathway B, Figure 1), previously observed with larger nanoparticles.<sup>[11b]</sup> To the best of our knowledge, the results reported herein for the Pd@MCF and Pd@MOF catalysts are unsurpassed in terms of TOF and selectivity (see the Supporting Information for details) by any heterogeneous Pd catalysts in the selective hydrogenation of cinnamaldehyde under ambient conditions (room temperature and 1 atm of H<sub>2</sub>). A review of recent literature on the topic revealed that only catalysts operating under much harsher conditions (up to 70  $^{\circ}$ C and up to 20 atm H<sub>2</sub>) manage to return higher turnover frequencies and comparable selectivities.

Next, the catalytic efficiency of Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and Pd<sup>0</sup>-AmP-MCF was compared for the chemoselective hydrogenation of crotonaldehyde (1 b) and methacrolein (1 c), which are challenging substrates but highly interesting, since butanal (2b) and isobutanal (2c) are industrially important chemical intermediates.<sup>[15]</sup> Although both catalysts had no difficulties in

Chem. Eur. J. 2016, 22, 7184-7189

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**Figure 1.** Unless otherwise noted, the reactions were performed on a 0.8 mmol scale, in 4 mL of acetone (0.2 M for Pd<sup>0</sup>-MlL-101-NH<sub>2</sub>(Cr)) or 2 mL of EtOAc (0.4 M for Pd<sup>0</sup>-AmP-MCF) at 20 °C and under H<sub>2</sub> atmosphere (balloon, 1 atm), for the indicated time. The progress of the reaction was monitored by <sup>1</sup>H NMR analysis of the crude reaction mixture. [a] The reaction was run in acetone in the presence of 0.1 equiv of K<sub>2</sub>CO<sub>3</sub>.

providing full conversions,  $Pd^{0}$ -AmP-MCF was found to be slightly faster while also affording excellent selectivity, even when using a loading of Pd as low as 0.5 mol%. On the other hand, the slightly lower selectivity of the Pd@MOF catalyst (95% and 90% for **2b** and **2c**, respectively) can be again attributed to the presence of Lewis acidic Cr sites on the framework, which are even more easily accessed by the small molecules of substrates **1b** and **1c**.

The selectivity was also excellent for linear  $\alpha_{,\beta}$ -unsaturated ketones. Both aromatic (1 d) and aliphatic (1 e) substrates were efficiently hydrogenated with complete selectivity by both catalysts, the reaction being faster for Pd<sup>0</sup>-AmP-MCF. Cyclic substrates (1 f–1 h) were also well tolerated even when the double bond was substituted (1 f and 1 h), and full conversions were achieved in a matter of minutes, displaying the versatility of these Pd nanocatalysts. Only trace amounts of alcohols 3 f–3 h were observed for Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) while Pd<sup>0</sup>-AmP-MCF provided the desired products 2 f–2 h with complete selectivity. However, in the case of the cyclic enone 1 g the formation of the over-reduced byproduct 3 g could be observed on prolonged reaction times. Gratifyingly, all products 2 b–2 h were

obtained in excellent yields and selectivities without the addition of base.

#### Stability and leaching

The initial recycling studies were conducted with the model substrate cinnamaldehyde (1 a), in the presence  $K_2CO_3$  and using Pd<sup>0</sup>-AmP-MCF as the catalyst. The reaction time was shortened to 30 min in order to clearly asses the catalyst efficiency for each cycle. During three consecutive cycles, a gradual decrease (67, 53 and 43%) in the conversion towards the desired product 2a was observed, although the selectivity was unchanged. Since the recycling of cinnamaldehyde was not optimal for Pd<sup>0</sup>-AmP-MCF, we did not evaluate the recyclability of Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) for this substrate. However, when ketone 1d was subjected to recycling studies, both Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and Pd<sup>0</sup>-AmP-MCF showed a very stable behavior with no differences in reactivity over five runs (Table 3). In each case, full conversion and excellent selectivity towards 2d were obtained after 75 min for Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and after 30 min for Pd<sup>0</sup>-AmP-MCF. Over the five runs, the amount of leached

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Pd was kept at barely detectable levels by ICP-OES ( $\leq$  0.2 ppm) for both catalysts (Table 3). The analysis of HAADF-STEM and TEM images of Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) revealed that in general, most nanoparticles retain their original size and shape (see Supporting Information, Figures S1 and S2). In the fresh catalyst about 85% of the nanoparticles fit in a very narrow size distribution range between 1.5 and 2.5 nm and altogether more than 95% of the nanoparticles are smaller than the pore size limit of the MOF (34 Å). After five recycling runs, some redistribution of Pd is observed but still about 87% of the nanoparticles remain under the size limit imposed by the MOFs pores. The other 13% of Pd nanoparticles, which are larger in size, are located on the surface of the MOF crystallites. This can happen due to Pd migration or degradation of the MOF by mechanical factors. Still, maintaining most of the Pd species in a very narrow size range shows that the porous support is actively protecting the catalyst against the natural Ostwald ripening and thus prolongs its lifetime. The XRPD patterns of fresh and recycled Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) after five runs were identical with no distinguishable loss in crystallinity (Supporting Information, Figure S3). However, small amounts of Cr were detected in the third and fifth run (Table 3), most likely caused by the mechanical stress to which the MOF crystals are subjected during reaction cycles under vigorous stirring.

Table 3. Metal leaching during recycling experiments. <sup>[a]</sup>							
	O Id	Pd cat 1 a Acetone 20 °C, 3	. (1 mol%) atm H₂ ∋ or EtOAc 60 or 75 min		d	$\bigcirc$	OH  3d
Pd <sup>0</sup> -MIL-101-NH <sub>2</sub> (Cr) Pd <sup>0</sup> -AmP-MCF							ICF
Run	Conv. of 1 d [%]	Selectivity 2 d/3 d	Pd leaching	Cr leaching	Conv. [%]	Selectivity 2 d/3 d	Pd leaching
			[ppiii]	[ppiii]			[ppiii]
1	>99	>99:1	< 0.1	0.1	>99	>99:1	< 0.1
2	>99	>99:1	n.d.	n.d.	>99	>99:1	n.d.
3	>99	>99:1	< 0.1	0.6	>99	>99:1	< 0.1
4	>99	>99:1	n.d.	n.d.	>99	>99:1	n.d.
5	>99	>99:1	0.1	1.8	>99	>99:1	0.2
[a] Conditions for reactions with $Pd^{0}$ -MIL-101-NH <sub>2</sub> (Cr): The reactions were performed on a 0.8 mmol scale, in 4 mL of acetone at 20 °C and under H <sub>2</sub> atmosphere (balloon, 1 atm), for 75 min. Conditions for reactions with $Pd^{0}$ -AmP-MCF: The reactions were performed on a 0.8 mmol scale, in 2 mL of EtOAc at 20 °C and under H <sub>2</sub> atmosphere (balloon, 1 atm), for 30 min. It was shown in the first run that the reaction of $Pd^{0}$ -AmP-MCF required at least 10 min for full conversion.							

When the Pd<sup>0</sup>-AmP-MCF was subjected to a similar HAADF-STEM and TEM analysis, a slightly wider size distribution was observed in the fresh catalyst with only 40% of the nanoparticles in the 1.5–2.5 nm range and 50% in the 2.5–3.5 nm range, while the remaining 10% of the nanoparticles were larger than 4 nm (see Supporting Information, Figures S4 and S5). This is not surprising considering the wider pore apertures of the MCF materials. However, we were delighted to find that after five recycling runs, the level of Pd agglomeration is barely detectable and most nanoparticles retain their size with ca. 90% of them remaining under 3.5 nm. This is in accordance with the previous results where Pd<sup>0</sup>-AmP-MCF had been used for hydrogenation of nitroarenes and no agglomeration was detected.<sup>[16]</sup>

## Conclusions

The two composite materials, Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) and Pd<sup>0</sup>-AmP-MCF have shown excellent activity in the selective hydrogenation of the C=C bond in various  $\alpha$ , $\beta$ -unsaturated carbonyl compounds, with all substrates reaching a full conversion within 90 min under only 1 atm of H<sub>2</sub>. Under the optimized reaction conditions, both Pd<sup>0</sup>-AmP-MCF and Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr) are able to prevent agglomeration of Pd nanoparticles, prolonging their lifetime and maintaining their size and facet dependent properties. This property provides both catalysts with a remarkable control of the chemoselectivity of the reaction, which is not achieved with commercially available Pd/C. Over multiple recycling runs the contamination of leached metallic species was kept at a minimum level. However, in this comparative study, Pd<sup>0</sup>-AmP-MCF proved to be slightly more effective than Pd<sup>0</sup>-MIL-101-NH<sub>2</sub>(Cr), and its excellent performance at low catalyst loadings makes it highly attractive for hydrogenations in industrial settings.

## **Experimental Section**

#### **General information**

Reagents and solvents were used as obtained from commercial suppliers without further purification, except cinnamaldehyde, which was distilled under reduced pressure before use.  $Pd^0$ -MIL-101-NH<sub>2</sub>(Cr) (8.40 wt%) and  $Pd^0$ -AmP-MCF (7.90 wt%) were synthesized according to previously reported procedures, described in the Supporting Information.

<sup>1</sup>H NMR spectra were recorded at 400 MHz on a Bruker Advance spectrometer. <sup>1</sup>H chemical shifts ( $\delta$ ) are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta_{\rm H}$  = 7.26 ppm). Elemental analysis: determinations of Pd and Cr were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian Vista MPX instrument. Medac Ltd. in the UK carried out the elemental analysis. Xray powder siffraction (XRPD) data were collected on a PANalytical X'Pert PRO diffractometer in reflectance Bragg–Brentano geometry equipped with a pixel detector and using  $Cu_{K\alpha 1}$  radiation. MIL-101 samples were suspended in EtOH, dispersed on zero-background Si plates and dried at room temperature. The morphology of "samples" was examined in a JEOL-2100F transmission electron microscope operated at 200 kV and equipped with a Schottky-type field emission gun. The crushed samples were dispersed in ethanol and then onto a TEM Cu grid with holey carbon supporting films. Bright-field and high-resolution TEM (HRTEM) images were recorded by a CCD camera (Gatan Ultrascan 1000). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), also known as Z-contrast, images for determining the size and distribution of Pd nanoparticles were acquired using a JEOL ADF detector. The probe size and camera length used are 0.20 nm and 8 cm, respectively.

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#### General procedure for the Pd<sup>0</sup>-catalyzed hydrogenation of enals and enones

The corresponding enal or enone (0.8 mmol) and Pd<sup>0</sup>-MCF/MOF (4–8.0  $\mu$ mol Pd, 0.50–1 mol%) were suspended in the chosen solvent (MCF: EtOAc, 2 mL or MOF: acetone, 4 mL) in a screw-capped Radley<sup>®</sup> tube. The reaction vessel was then evacuated and filled with hydrogen gas from a balloon in three repeating cycles. The reaction was allowed to stir at room temperature for the indicated time with the H<sub>2</sub> balloon attached, after which the reaction was stopped. Aliquots were taken from the reaction mixture, filtered through Celite, eluted with CDCl<sub>3</sub> (1 mL), and analyzed by <sup>1</sup>H NMR spectroscopy to determine the conversion and selectivity. See the Supporting Information for more details.

## Acknowledgements

The Swedish Research Council (VR), the Swedish Governmental Agency for Innovation Systems (VINNOVA), the Berzelii Center EXSELENT, and the Knut and Alice Wallenberg Foundation are gratefully acknowledged for project grants. The Knut and Alice Wallenberg Foundation is also acknowledged for an equipment grant for the electron microscopy facilities at Stockholm University. The help of Dr. Fabian Carson for measuring XRPD patterns at Stockholm University is gratefully acknowledged.

**Keywords:** heterogeneous catalysis • mesocellular foam • metal–organic framework • palladium nanoparticles • selective hydrogenation

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Received: February 24, 2016 Published online on April 25, 2016