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# Solvent-Driven Selectivity Control to either Anilines or Dicyclohexylamines in Hydrogenation of Nitroarenes over a Bifunctional Pd/MIL-101 Catalyst

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# Abstract

The hydrogenation of nitroarenes is one of the most important strategies to produce corresponding anilines and dicyclohexylamines, both of which are the fundamental raw materials in the synthesis of various pharmaceuticals and fine chemicals. Nevertheless, it is still a great challenge to develop highly versatile and flexible catalytic system to selectively generate desired amines. Herein, we report the solvent-driven selectivity control over a bifunctional Pd/MIL-101 catalyst for the hydrogenation of nitrobenzene. An almost full selectivity of 99.9 % to aniline or a surprising selectivity of 99.1 % to dicyclohexylamine is achieved by using dimethyl formamide (DMF, a polar solvent) or n-hexane (an apolar solvent) as the solvents, respectively. It is proposed that the polarity of solvents can effectively regulate the

linkage between reactants/intermediates and Pd/MIL-101, affording controllable selectivities of aniline or dicyclohexylamine at will. Besides, the Lewis acid sites in Pd/MIL-101 can also effectively activate the aromatic ring and accelerate the cross coupling reaction of amine. This solvent-driven catalytic system also exhibits good recyclability and compatibility for a wide substrate scope in both DMF and n-hexane, showing great promise for industrial applications. This study might open an avenue for the hydrogenation of nitroarenes to selectively produce anilines or dicyclohexylamines by simply regulating the solvent polarity over a bifunctional catalyst system.

KEYWORDS: Pd/MIL-101; selective hydrogenation; nitrobenzene; aniline; dicyclohexylamine

# 1. Introduction

The hydrogenation of nitroarenes is one of the most important synthetic paths for producing corresponding N-containing products, such as anilines, azoxy and secondary amines, which are widely used as intermediates in the synthesis of dyes, pharmaceuticals and fine chemicals.<sup>1-7</sup> Although extensive efforts have been made to develop various catalytic systems for efficient transformation of nitroarenes,<sup>8-15</sup> most of them are focused on the hydrogenation of nitro compounds to anilines. Up to date, there are only few reports on the reduction of aromatic ring or the cross coupling reaction of amino groups, because harsh operation conditions or/and bifunctional or multifunctional catalysts are usually required for these purposes.<sup>16-22</sup> In this regard, Muller *et al.* recently reported that a highly selective conversion of nitrobenzene (NB)

to cyclohexylamine (CA) could be achieved over a Ru/CNTs catalyst under 100 bar hydrogen pressure and 140 °C reaction temperature.<sup>17</sup> Corma *et al.* also showed that nitroderivatives were transformed to cyclohexylanilines in good selectivities by using a Pd/C catalyst system with Bronsted acid as cocatalyst.<sup>18</sup> Nevertheless, to the best of our knowledge, there is still no catalyst system reported so far that can transform nitroarenes into dicyclohexylamines with excellent selectivities. Furthermore, the controllable conversion of one nitroarene compound into multi-target products via single catalyst system remains a great challenge.

Metal-organic frameworks (MOFs) are a new class of porous materials possessing large internal surface areas, well-defined structures, and tunable chemical properties.<sup>23-26</sup> Owing to these features, MOFs have received tremendous attentions in the applications of heterogeneous catalysis, particularly when they are used as the supports for noble metal (e.g., Pd, Au, Ru, and Pt) nanoparticles (MNPs).<sup>27-36</sup> On the one hand, the open and uniform channels of MOFs make them particularly suitable for the efficient immobilization of MNPs, thus effectively avoiding the loss of MNPs and vastly exposing the active sites.<sup>25,33</sup> On the other hand, the organic linkers or the metal nods of MOFs can also be used as unique functional moieties, and the interaction between MNPs and MOFs might offer the opportunity for MNPs/MOFs to be bifunctional even multifunctional catalysts.<sup>28,37</sup> Based on these advantages, MOF-immobilized MNPs have been extensively studied in a wide range of chemical transformations over the past few years.<sup>27-31</sup> Our group has also made some contributions in this topic, developing a series of novel metal-NPs@MOFs for

efficient transformations, e.g., one-step conversion of acetone to methyl isobutyl ketone,<sup>28</sup> selective hydrogenation of nitriles to imines,<sup>29</sup> effective hydrogenation of biomass derived furfural to cyclopentanone,<sup>31</sup> and selective oxidation of cinnamyl alcohol.<sup>32</sup>

In this work, as shown in Figure 1, we report the controllable selective hydrogenation of nitroarenes over a heterogeneous catalytic system based on ultra-tiny Pd NPs immobilized in a chromium-based MOF, namely MIL-101  $(Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O, n \approx 25)$ ,<sup>38-40</sup> by using a colloidal deposition method. In the MIL-101 structure, the potential unsaturated chromium sites (up to 3.0 mmol·g<sup>-1</sup>) can provide a large number of Lewis acidic sites after the removal of terminal water molecules, which has been proved to play significant role in the activation of aromatic compounds.<sup>40</sup> Thus, after loading Pd NPs, these two types of hydrogenation active ingredients would work cooperatively to show a bifunctional catalytic activity. Consequently, Pd/MIL-101 is capable of catalyzing the selective hydrogenation of nitroarenes to either anilines or dicyclohexylamines just by using different solvents, whose polarity is the key factor for obtaining the controllable selectivities to anilines *vs* dicyclohexylamines.

#### 2. Experimental

# 2.1. Catalyst preparation

All chemicals were purchased from commercial sources and used without further treatments. All solvents were analytical grade and distilled prior to use.

2.1.1 Synthesis of Pd/MIL-101

#### ACS Catalysis

MIL-101 was prepared according to the previous reported procedures.<sup>38</sup> Typically, the hydrothermal reaction of  $Cr(NO_3)_3 \cdot 9H_2O$  (0.80 g, 2 mmol), terephthalic acid (0.33 g, 2 mmol), HF (48 wt %, 2 mmol), and 10 mL deionized water were carried out at 220 °C for 8 h. The mixture was cooled first to 150 °C in 1 h, and then slowly to room temperature in 12 h. Subsequently, the mixture was first filtrated by using a large pore fritted glass filter (2, Schott) to isolate large terephthalic acid crystal, and then filtrated in a small pore paper filter (1°, Whatman) to remove the free terephthalic acid. The obtained green MIL-101 powder was soaked in ethanol (95 % EtOH with 5 % water) at 80 °C for 24 h followed by filtrating the hot solution. The solid was finally dried at 150 °C under vacuum for 24 h.

MIL-101-supporting palladium catalyst was prepared via a colloidal deposition method.<sup>41</sup> In a typical synthesis, a methanol solution of  $Pd(NO_3)_2 \cdot 2H_2O$  (0.001 M) was first prepared with PVP (polyvinylpyrrolidone) as a protecting agent (Pd:PVP monomer = 1:10, molar ratio) and vigorously stirred for 1 h. Then, a desired amount of NaBH<sub>4</sub> (Pd:NaBH<sub>4</sub> = 1:5, molar ratio) was added to the solution to obtain a dark brown sol. After few minutes sol generation, an appropriate amount of activated MIL-101 powder was added to the colloidal solution, which was stirred for 24 h. The as-synthesized sample was dried at 100 °C under vacuum for 2 h and then treated in a stream of H<sub>2</sub> at 200 °C for 2 h to yield Pd/MIL-101. The Pd loading on the sample was 2 wt %.

2.1.2 Synthesis of Pd/ZIF-8, Pd/HKUST-1, and Pd/UIO-66

ZIF-8, HKUST-1, and UIO-66 were prepared according to precious reports.<sup>33, 42, 43</sup>

And Pd/ZIF-8, Pd/HKUST-1, and Pd/UIO-66 were prepared via the same path and with the same loading amount as the preparation of Pd/MIL-101 except using different supports.

2.1.3 Synthesis of Pd/SiO<sub>2</sub> and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were obtained from commercial source. Pd/SiO<sub>2</sub> and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared by an impregnation method. Typically, a certain amount of support (SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was dispersed in 20 mL of acetone, which was stirred for 30 min at room temperature. Subsequently, a methanol solution of Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (0.001 M) was added dropwise to the above solution under vigorously stirring for 10 min. After being subjected to ultrasonication for 20 min, the slurry was then stirred at room temperature for 24 h. The impregnated samples were washed with acetone for a few times and dried slowly at room temperature followed by treating at 150 °C for 8 h under vacuum. The Pd<sup>2+</sup> in as-synthesized samples was subsequently reduced to Pd<sup>0</sup> in a stream of H<sub>2</sub> at 200 °C for 2 h to obtain Pd/SiO<sub>2</sub> and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Pd loading on both samples were 2 wt%.

#### 2.2. Characterization

Powder X-ray diffraction patterns of the samples were obtained by a Rigaku diffractormeter (D/MAX-IIIA, 3 kW) using Cu K $\alpha$  radiation (40 kV, 40 mA,  $\lambda$  = 0.1543 nm). The N<sub>2</sub> adsorption/desorption isotherms were measured by a Micromeritics ASAP 2020M instrument at 77 K, and the samples were evacuated at 150°C overnight before the analysis. The palladium loadings of the samples were measured quantitatively by atomic absorption spectroscopy (AAS) on a Hitachi

Z-2300 instrument. The morphology and nanoparticle size of samples as well as the element mapping were investigated by using a scanning electronic microscope (SEM, Hitachi SU8220) and a transmission electron microscope (TEM, JEOL, JEM-2100F and JEM-1400) with energy-dispersive X-ray spectroscopy (EDS) analysis at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific K-ALPHA system with a base pressure of  $2 \times 10^{-9}$  mbar.

# 2.3. Catalytic Reaction

The nitrobenzene hydrogenation process was conducted in a 10 mL Teflon-lined stainless steel autoclave equipped with a pressure gauge under the magnetic stir. Typically, nitroarenes (0.5 mmol), catalyst (1.0 mol%, based on Pd content), and 4 ml of solvent were added to the autoclave and the mixture was stirred at 600 rpm. The autoclave was purged ten times with H<sub>2</sub>, and then pressurized with H<sub>2</sub> to the required pressure and heated up to the target temperature. After reaction, the products were quantified and identified by a GC-MS (Agilent Technologies 7890B-5977A equipped with a 0.25 mm  $\times$  30 m HP- 5MS capillary column) with dodecane as an internal standard (Figure S1-S3).

The conversion of NB and the selectivity and yield of the products (aniline (AN), cyclohexylamine (CA), phenylcyclohexylamine (PC) and dicyclohexylamine (DA)) were calculated based on following equations:

$$Con.(NB) = \frac{\sum xC(i)}{C(NB) + \sum xC(i)} \times 100\%$$
$$Sel.(i) = \frac{xC(i)}{\sum xC(i)} \times 100\%$$

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$$Yield(i) = Sel.(i) \times Con.(NB) \times 100\%$$

where *C* represents the concentrations of the products, *i* represents one of AN, CA, PC and DA, and *x* means the benzene ring numbers in one product molecule.

For the recyclability test, the catalyst was separated from the reaction solution, washed with acetone, and dried for the next run.



Figure 1. Schematic illustration of the selective hydrogenation of nitrobenzene over

the bifunctional Pd/MIL-101 containing Lewis acid sites and Pd NPs.



Figure 2. (a) PXRD patterns of simulated MIL-101, as-synthesized MIL-101, and Pd/MIL-101; (b)  $N_2$  adsorption-desorption isotherms of as-synthesized MIL-101 and Pd/MIL-101.

# 3. Results and discussion

MIL-101 was synthesized and activated under vacuum according to the reported procedure with some modifications.<sup>38</sup> Subsequently, Pd NPs were generated and immobilized on MIL-101 to prepare the Pd/MIL-101 catalyst by using a colloidal deposition method. Here, the loading amount of Pd was fixed to 2 wt % and the actual value was measured by atomic absorption spectrum (AAS) (Table S1). Powder X-ray diffraction (PXRD) was used to characterize the crystallinity of the prepared catalyst. As shown in Figure 2a, Pd/MIL-101 matches well with both the simulated and as-synthesized MIL-101, indicating the crystallinity and structure of MIL-101 are well retained after loading of Pd NPs.<sup>41</sup>



Figure 3. (a, c) TEM, (b) STEM and (d) HR-TEM images of the Pd/MIL-101. (e)

HAADF-STEM image and the corresponding elemental mappings of the Pd/MIL-101.

The inset of (c) is the size distribution of Pd NPs.

Then, the surface areas and pore volumes of MIL-101 and Pd/MIL-101 were measured by N<sub>2</sub> adsorption/desorption at 77 K (Figure 2b). Both samples exhibit similar type I isotherms with high surface areas of 2658  $m^2g^{-1}$  and 2092  $m^2g^{-1}$  for MIL-101 and Pd/MIL-101, respectively, further indicating the ordered porous structure of Pd/MIL-101 are well inherited from the MIL-101 support.<sup>41</sup> The appreciable decrease in N2 adsorption amount after the introduction of Pd NPs can be attributed to the partial blockage of the cavities in Pd/MIL-101 by the deposited Pd NPs. SEM image (Figure S4) also reveals that the octahedral shape of MIL-101 can be well preserved after the loading of Pd NPs. The detailed structure of Pd/MIL-101 was further investigated by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). As shown in Figure 3a-c and S5, a large number of small NPs are homogeneously distributed on an octahedron matrix with a mean diameter of  $2.56 \pm 0.72$  nm, where no remarkable formation of aggregates can be observed. High-resolution TEM (HR-TEM) image shows that the interplanar spacing of the particle lattices is about 0.225 nm, corresponding to the (111) plane of face-centered cubic Pd (Figure 3d).<sup>41</sup> A representative high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) image and the corresponding EDS mappings are shown in Figure 3e. From the selected area, the uniform distributions of Cr, C and Pd elements are observed in the same area, further confirming that Pd NPs are effectively deposited on MIL-101 matrix with potential interaction between Pd NPs and the support. X-ray photoelectron spectroscopy (XPS)

was further used to study the chemical state of Pd in Pd/MIL-101. As shown in Figure S6, Pd/MIL-101 shows two obvious peaks at 335.5 and 340.8 eV, which can be ascribed to the binding energies of Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  of zero-valent Pd, respectively, indicating that Pd in this sample is in its metallic state.<sup>44</sup>

The hydrogenation reaction of NB was subsequently conducted over Pd/MIL-101 (reaction conditions: 120  $^{\circ}$ C, 0.6 MPa of H<sub>2</sub> and 4 ml of selected solvents). In order to investigate the influence of solvent on the reaction, a series of solvents with different polarities were first used to perform the reaction. The solvents we chose here are methanol (MeOH), ethanol (EtOH), N, N-dimethylformamide (DMF), tetrahydrofuran (THF) and n-hexane. The polarity of these solvents is estimated by the dielectric constant listed in Table 1,<sup>45, 46</sup> whose order is DMF > MeOH > EtOH > THF >n-hexane. A complete conversion of NB is achieved in all solvents listed in Table 1 (entries 1-6), confirming the high catalytic activity of Pd/MIL-101 for the reduction of aromatic nitro group. Note that aniline (AN) is the only product when using DMF as the solvent (Table 1, entry 1). The kinetic curves of Pd/MIL-101 for this reaction in DMF solvent show that AN is the only detected product and diazo intermediates are not detected in the whole reaction process, indicating the aromatic nitro compound is reduced via a direct route (Figure 4a).<sup>47</sup> However, with a decrease in the polarity of solvents, the selectivities of AN over Pd/MIL-101 also decrease sharply from >99.9 % in DMF to 64.2 % in MeOH, and then 28.8 % in EtOH (Table 1, entries 2-3). Besides AN, other products, namely cyclohexylamine three (CA), phenylcyclohexylamine (PC) and dicyclohexylamine (DA), are also observed in these

systems. Further decreasing the polarity, the selectivity of AN can be further decreased to almost 0 % in both THF and n-hexane (Table 1, entries 4-5). Interestingly, in contrast to AN, the selectivities of DA over Pd/MIL-101 increase with decrease in solvent polarity, thus following the order of MeOH < EtOH < THF < n-hexane (Figure 5 and entries 2-6 of Table 1). It is noteworthy that 99.1 % selectivity of DA can be obtained when using n-hexane as the solvent, which is also the highest value among all the previously reported systems.<sup>4, 18, 48, 49</sup> Clearly, the high activity and solvent-driven selectivity of our system show great promise for industrial applications.



**Figure 4.** The kinetics curves for the hydrogenation of NB under 120 °C and 0.6 MPa of  $H_2$  with (a) DMF and (b) n-hexane as the solvents.

Encouraged by these results, we further investigated the kinetic curves of Pd/MIL-101 in this reaction using n-hexane as solvent. As shown in Figure 4b, four products, AN, CA, PC and DA are all detected in the reaction process. In the initial stage, AN is emerged as the main product, but rapidly decreases as the reaction progresses, indicating it can be further hydrogenated easily when using n-hexane as the solvent. In the meantime, a small amount of CA, generally regarded as the product from the hydrogenation of aromatic ring in AN, is observed although its selectivity is

always below 10 % with the reaction going on, implying that CA is also an active intermediate product. In addition, a certain amount of PC is also formed in the early stage, which is originated from the cross coupling reaction of AN and CA. The amount of PC is cumulative to the maximum at  $\sim$ 1 h, and then gradually decreases due to its transformation to DA, which also confirms that DA mainly results from the hydrogenation of PC rather than the cross coupling reaction of two molecules of CA.



**Figure 5.** Selective hydrogenation of nitroarenes to either aniline (AN) or dicyclohexylamine (DA) over a bifunctional Pd/MIL-101 catalyst.

For comparison purposes, some other MOFs supported catalysts, such as Pd/ZIF-8, Pd/HKUST-1, and Pd/UiO-66, and traditional porous materials supported Pd NPs, like Pd/SiO<sub>2</sub> and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were also prepared (their Pd loadings are also in the range of 1.7-1.9 wt %) and their catalytic performances for this reaction were then investigated (Figure S7-S11, Table S1). As shown in Table 1 (entries 6-15), full conversion of NB can be achieved over these catalysts in both DMF and n-hexane, and AN is also the only product when the reaction is conducted in DMF (entries 6, 8, 10, 12 and 14). Unfortunately, when using n-hexane as the solvent, Pd/SiO<sub>2</sub> provides

no selectivity of DA (Table 1, entry 7) and Pd/y-Al<sub>2</sub>O<sub>3</sub> shows only 19.5 % selectivity to DA (Table 1, entry 9), although both of them also contain solid acid. ZIF-8 and HKUST-1 are widely used as supports due to their high specific surface area and pore volume.33, 42 However, Pd/ZIF-8 and Pd/HKUST-1 just exhibit very poor solvent-driven performances with only 11.1 % and 5.2 % selectivities to DA observed in n-hexane, respectively (Table 1, entries 11, 13). Furthermore, Pd/UiO-66 shows a moderate catalytic performance, giving 56.0 % selectivity of DA in n-hexane (Table 1, entry 17), which might be attributed to its analogous construction with Pd/MIL-101 with slightly lower surface area and Lewis acidic sites derived from unsaturated Zr<sup>4+</sup> sites.<sup>43</sup> These results directly demonstrate that only by integrating both of high surface area and Lewis acid can the Pd/MIL-101 catalyze the solvent-driven selective hydrogenation of NB to either AN or DA through controlling the aromatic ring hydrogenation and cross coupling reaction in different solvents.

$ \underbrace{ \bigvee}_{H_2}^{NO_2} \xrightarrow{Cat.} + \underbrace{ \bigvee}_{H_2}^{NH_2} \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2} \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2} \underbrace{ \bigvee}_{H_2}^{H_2} + \underbrace{ \bigvee}_{H_2}^{H_2}  $									
	NB		AN	CA	PC		DA		
Entry	Catalyst	Solvent	Dielectric	Time	Con. (%)		Sel. (	(%) <sup>b</sup>	
			constant (ε)	(h)		AN	CA	PC	DA
1	Pd/MIL-101	DMF	38.3	6	100	>99.9	-	-	-
2	Pd/MIL-101	MeOH	33.6	10	100	64.2	1.3	13.4	21.1
3	Pd/MIL-101	EtOH	25	10	100	28.8	0.7	29.3	41.2
4	Pd/MIL-101	THF	7.58	15	100	-	4.3	10.2	85.5
5	Pd/MIL-101	n-hexane	1.89	8	100	-	0.9	-	99.1
6	Pd/SiO <sub>2</sub>	DMF	38.3	12	100	>99.9	-	-	-
7	Pd/SiO <sub>2</sub>	n-hexane	1.89	8	100	>99.9	-	-	-
8	$Pd/\gamma$ - $Al_2O_3$	DMF	38.3	12	100	>99.9	-	-	-

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9	$Pd/\gamma$ - $Al_2O_3$	n-hexane	1.89	15	100	49.6	4.2	26.7	19.5
10	Pd/ZIF-8	DMF	38.3	10	100	>99.9	-	-	-
11	Pd/ZIF-8	n-hexane	1.89	12	100	64.7	5.6	18.6	11.1
12	Pd/HKUST-1	DMF	38.3	10	100	>99.9	-	-	-
13	Pd/HKUST-1	n-hexane	1.89	12	100	76.5	4.8	13.5	5.2
14	Pd/UiO-66	DMF	38.3	8	100	>99.9	-	-	-
15	Pd/UIO-66	n-hexane	1.89	15	100	20.9	3.3	19.8	56.0

<sup>a</sup>Reaction conditions: 0.5 mmol NB, Pd catalysts (1.0 mol% of Pd relative to NB), 4 ml of solvents, 120  $^{\circ}$ C, and 0.6 MPa of H<sub>2</sub>.

<sup>b</sup>The selectivity was calculated based on benzene ring.

On the basis of the above results, we propose a plausible reaction mechanism to explain the solvent-driven hydrogenation of nitrobenzene over Pd/MIL-101 (Figure 6). First, because of its strong electron-withdrawing behavior, the nitro group of nitrobenzene can strongly coordinate with the surface of Pd NPs, and then is directly reduced to aminobenzene (AN) by dissociated H<sub>2</sub> absorbing on Pd NPs.<sup>17</sup> It is worth to note that the aromatic ring in nitrobenzene is electron deficient, but become electron rich in AN.<sup>50</sup> Thus, it is presumed that the linkage between Pd/MIL-101 and the electron-rich aromatic ring can be tremendously influenced by the polarity of the solvent. When the reaction proceeds in solvents with strong polar (like DMF), the as-obtained AN can easily desorb from the catalyst surface and be released as the final product. On the contrary, when using nonpolar n-hexane as the solvent, the initially-produced AN can adsorb strongly on Pd NPs. Consequently, the aromatic ring of AN can be activated by the Lewis acidic sites (i.e.,  $Cr^{3+}$ ) in MIL-101,<sup>51</sup> which accelerate the reduction of AN to CA. Then, the cross coupling reaction of AN and CA is motivated to produce PC by following a "hydrogen-borrowing" 18, 22, 52, 53

mechanism: firstly, the dehydrogenation of CA to an imine would occur; then the resultant imine can react with AN by nucleophilic attack to generate an unstable aminoaminal; finally, after the release of an ammonia (Figure S12), the corresponding secondary imine is formed, which is subsequently hydrogenated to produce PC. From the kinetic curve in Figure 4b, we can see that this process is quick and efficient, which might be attributed to the synergistic effect of Pd NPs and MIL-101. On the one hand, Pd NPs have been previously demonstrated to be able to stimulate some dehydrogenation and hydrogenation reactions.<sup>8, 54</sup> On the other hand, the Lewis acidic sites in MIL-101 can not only activate the imine, but also quench the released ammonia and therefore promote the cross coupling reaction.<sup>3</sup> Finally, the generated PC is further hydrogenated to produce DA with very high yield.



**Figure 6.** The proposed routes for the hydrogenation of NB in polar or apolar solvent over Pd/MIL-101.



**Figure 7.** Reuses of the Pd/MIL-101 for the hydrogenation of NB in (a) DMF and (b) n-hexane by using short reaction times of 20 and 10 min, respectively.

The recyclability of the Pd/MIL-101 was further investigated in both DMF and n-hexane under the identical reaction condition. After reaction, the catalyst was separated from the reaction solution, washed and dried for the next run. As shown in Figure 7a, only a slight decrease of NB conversion is observed in DMF after the 6<sup>th</sup> run, while its selectivity to AN remains nearly unchanged. Similarly, the conversion of NB can be also well retained after the 6<sup>th</sup> run when using n-hexane as the solvent (Figure 7b). PXRD patterns show that the diffraction peaks of the used Pd/MIL-101 are all well matched with the fresh one (Figure S13), suggesting that the structural integrity of Pd/MIL-101 can be well preserved after recycling tests. Moreover, the octahedral shape of Pd/MIL-101 is also well preserved regardless of the solvents used as exhibited by SEM images (Figure S4 and S14a, d). In addition, only slight aggregation of Pd NPs is observed in the TEM images of reused catalysts even after six catalytic runs (Figure S14b, c, e and f). These results further confirm the good stability and recyclability of the Pd/MIL-101 for this reaction.

Table 2. Catalytic hydrogenation of various substituted nitrobenzenes over the Pd/MIL-101





		NO <sub>2</sub> Pd/MIL	-101		H <sub>2</sub>	
	R	H <sub>2</sub> (0.6 N	76) 7 1Pa) n-hexane		$\mathcal{A}_{R}$	
Number	Substrates	Solvents	Products	Reaction time (h)	Con. (%)	Sel. (%)
	NO <sub>2</sub>	DMF	NH <sub>2</sub>	6	100	>99.9
1		n-hexane	$\bigcirc {}^{\sharp} \bigcirc$	8	100	99.1
2	NO <sub>2</sub>	DMF	H NH <sub>2</sub>	6	100	>99.9
		n-hexane		12	100	94.5
3	NO <sub>2</sub>	DMF	NH <sub>2</sub>	6	100	>99.9
5		n-hexane		12	100	94.1
4		DMF	NH <sub>2</sub>	6	100	>99.9
4		n-hexane		12	100	92.1
5	NO:	DMF	NH <sub>2</sub>	8	95.4	>99.9
5		n-hexane		15	100	86.7
		DMF	NH <sub>2</sub>	8	97.3	>99.9
6	I	n-hexane	$\begin{array}{c} \downarrow {}^{k} \\ \downarrow \end{array}$	15	100	88.5
7	NO <sub>2</sub>	DMF	NH <sub>2</sub>	8	95.4	>99.9
1		n-hexane		15	100	88.1
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<sup>a</sup>Reaction conditions: 0.5 mmol of substrates, Pd/MIL-101 (1.0 mol% Pd relative to substrates), 4 ml of selected solvents, 120 °C, and 0.6 MPa of  $H_2$ .

Finally, several aromatic nitro compounds containing various alkanes were also investigated over Pd/MIL-101 with the optimized conditions in both DMF and n-hexane. As summarized in Table 2, all the investigated nitroarenes can be selectively hydrogenated to their corresponding anilines or dicyclohexylamines by simply using DMF or n-hexane as the solvent, demonstrating the good tolerance of Pd/MIL-101 to different substrates. Nevertheless, the yields of both anilines and dicyclohexylamines decrease slightly with the complexification of alkanes, which might be ascribed to the influence of steric effect.

#### 4. Conclusions

In summary, we have demonstated that Pd/MIL-101 featuring encapsulated Pd NPs in the pores of MIL-101 with abundant Lewis acidic sites can be used as a bifunctional catalyst for the solvent-driven selective hydrogenation of nitrobenzene to either aniline or dicyclohexylamine at will. The key to success for this controllable system is the use of the solvent polarity as an effective strategy to regulate the linkage between reactants/intermediates and Pd/MIL-101. In addition, the synergetic effect of

Pd NPs and MIL-101 can also effectively elevate the aromatic ring hydrogenation as well as the cross coupling reaction of amines. Consequently, an almost full selectivity to aniline is obtained in DMF (a polar solvent), and a surprising selectivity of 99.1 % to dicyclohexylamine is achieved in n-hexane (an apolar solvent). Furthermore, this solvent-driven catalytic system is also confirmed for a wide substrate scope and thus provides a facile strategy for the hydrogenation of nitroarenes to selectively produce anilines or dicyclohexylamines.

## ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Additional SEM and TEM images, XPS spectra, XRD patterns, AAS results,

optical photographs, and MS spectra.

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# Notes

The authors declare no competing financial interest.

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Dicyclohexylamine (DA)

