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# Ultrasmall palladium nanoparticles supported on amine-functionalized SBA-15 efficiently catalyze hydrogen evolution from formic acid<sup>†</sup>

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The success of the so-called "hydrogen economy" for large-scale applications will ultimately depend on efficient and sustainable production, storage and distribution of hydrogen. Owing to its low toxicity, high volumetric H<sub>2</sub> storage capacity and availability both from renewable resources (e.g., biomass) and non-renewable resources (e.g., fossil fuel feedstocks), formic acid is one of the most favorable chemical hydrogen storage media for large-scale energy storage applications. However, for FA to become a viable hydrogen storage medium, efficient catalysts that enable it to release H<sub>2</sub> at low cost are necessary. Herein we report a facile synthetic route to amine-functionalized nanoporous silica-supported ultrasmall Pd nanoparticles (SBA-15-Amine/Pd) that are highly active catalysts for formic acid dehydrogenation, producing hydrogen at ambient temperature with a high turn-over-frequency (TOF) of 293 h<sup>-1</sup>, which is among the highest TOFs ever reported for the reaction by a heterogeneous catalyst. We also show that the material is easily recyclable multiple times, without losing its catalytic activity. So, the catalyst we developed can be expected to be part of the solutions of our sustainability challenges.

Given the current energy landscape, where the consumption of fossil fuels continues to rise while the negative environmental impacts associated with burning fossil fuels continue unabated, the search for alternative, benign and sustainable energy sources is of burgeoning interest. In this context, hydrogen—as one of the most promising clean energy carriers—can play pivotal roles in meeting these challenging issues, as already successfully demonstrated with clean hydrogen-fed fuel cell technologies.<sup>1-4</sup> Despite the progress made since the 1970s, when the term "hydrogen economy" was coined by Bockris,<sup>2</sup> it has become apparent that the ultimate success of the hydrogenbased energy cycle for large scale applications heavily hinges on efficient, large-scale production, storage, and distribution of hydrogen. In particular, the development of safe and reversible hydrogen storage systems is a key technical issue that must be fully addressed to successfully realize an "ideal" hydrogen economy.<sup>5-7</sup>

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Because of its low toxicity, high hydrogen storage capacity and availability both from renewable resources (*e.g.*, biomass) and non-renewable resources (*e.g.*, fossil-feedstock), formic acid (FA) has recently attracted significant attention for its potential applications as a chemical hydrogen storage medium.<sup>8,9</sup> FA's high volumetric  $H_2$  storage capacity of 53 g L<sup>-1</sup> particularly makes it advantageous for many on-board energy applications.<sup>10</sup> Moreover, in presence of suitable catalysts, FA can be dehydrogenated to produce the hydrogen it carries under ambient conditions, making it auspicious for direct utilization within hydrogen-fed polymer electrolyte membrane-based fuel cells (PEMFCs).

For FA to be used as a viable hydrogen storage medium though, efficient catalysts that enable it to generate  $H_2$  at low cost are critically needed. In recent years, various homogeneous catalysts based on metals such as Ru<sup>11-14</sup> and Ir<sup>15</sup> and heterogeneous catalysts including AuPd/C,<sup>16</sup> AgPd,<sup>17</sup> CoAuPd/C,<sup>18</sup> Pd/ C<sub>3</sub>N<sub>4</sub><sup>19,20</sup> for the dehydrogenation of FA have been reported. Generally, homogeneous catalysts are highly active and exhibit higher turnover frequencies (TOFs) than heterogeneous catalysts for many reactions including formic acid dehydrogenation. However, the heterogeneous catalysts are advantageous over homogeneous ones in terms of recoverability of the spentcatalysts from the reaction mixtures.<sup>21</sup> By immobilizing homogeneous catalysts onto solid support materials, the benefits attainable by both types of catalysts can sometimes be realized. This approach of 'heterogenization of homogeneous catalysts'

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can also be successfully applied for catalytically active ultrasmall metallic nanoclusters, which have increasingly become promising catalysts for formic acid dehydrogenation.<sup>22-26</sup> Furthermore, functional groups such as amines could easily be supported on the surfaces of such heterogeneous catalysts to serve as interaction sites for supported metallic nanoclusters as well as co-catalytic species, which in the case of FA-dehydrogenation can function as deprotonation sites for FA molecules, synergistically assisting FA's catalytic dehydrogenation. This hypothesis, in conjunction with the recent successful demonstration of silica nanosphere-encapsulated Au nanoparticles<sup>26</sup> and silica microsphere<sup>22</sup> and metal-organic framework (MOF)<sup>24</sup> supported Pd catalysts for FA dehydrogenation, has prompted us to explore other related but different systems. This has ultimately led us to synthesize hybrid catalytic systems composed of ultrasmall Pd nanoparticles (Pd NPs)/amine-functionalized mesoporous silica, as shown in Scheme 1, that can efficiently catalyze FA dehydrogenation.

First, SBA-15 type mesoporous silica was synthesized using a supramolecular self-assembly synthetic method, as demonstrated by Zhao et al.27 By using the residual surface silanols (≡Si-OH) located on the pore walls of SBA-15, the material was functionalized with organic functional groups, which were then utilized to anchor metal ions onto the surfaces of the nanoporous material.28,29 In this current effort, primary amine groups were anchored on SBA-15 by grafting (3-aminopropyl)triethoxysilane (APTES) onto the surfaces of SBA-15, producing a material denoted as SBA-15-Amine (Scheme 1). Then, Pd<sup>2+</sup> ions were supported onto the surfaces of SBA-15-Amine by mixing the latter with ammoniacal palladium solution (Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>).<sup>30</sup> Subsequent reduction of the resulting material using a H<sub>2</sub>/N<sub>2</sub> mixture (1 : 9 v/v) at 250 °C for 3 h afforded SBA-15-Amine-supported Pd NPs (denoted hereafter as SBA-15-Amine/Pd) that are highly catalytically active for FA dehydrogenation (see detailed experiments in the ESI<sup>†</sup>).

The structure and morphology of SBA-15-Amine/Pd were first analyzed by high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The Pd nanoparticles in SBA-15-Amine/Pd were found to be ultrasmall, having an average size of 1.9 nm (Fig. 1a and b). In contrast, the unmodified SBA-15/Pd prepared under

otherwise identical synthetic conditions afforded bigger Pd NPs (Fig. 1c and d). The latter is not surprising since ultrasmall Pd NPs are often too difficult to obtain with conventional reduction methods employing NaBH<sub>4</sub> and/or without capping agents because they tend to aggregate easily due to their relatively high surface energies. In another control experiment, the Pd NPs formed following the reduction of the ammoniacal Pd(II) species in the absence of SBA-15-Amine were also, unsurprisingly, significantly bigger in size, having particle sizes as high as 150 nm (Fig. S2†). Thus, the presence of amine functional groups inside the mesoporous silica channels and their ability to stabilize the Pd NPs must have played important roles in keeping the Pd NPs quite small during the reduction of Pd<sup>2+</sup> ions under H<sub>2</sub> at 250 °C. The amounts of Pd in the SBA-15-Amine/Pd and SBA-15/Pd, as characterized by ICP-AES, were found to be identical (0.32 mmol  $g_{cat}^{-1}$ , 3.4 wt%). On the basis of a previous report,<sup>31</sup> it is conceivable that the amine functional groups grafted in our SBA-15-Amine/Pd could serve as Brønsted basic sites, facilitating the deprotonation of FA into a formate intermediate, while the ultrasmall Pd NPs around them catalytically activate the C-H bond of the resulting formate species. Besides this, the amine groups help with the formation as well as the stabilization of the ultrasmall Pd NPs (by protecting them from aggregation during the catalytic reactions (see below)).

Furthermore, the amine groups supported onto SBA-15 can donate electron density to Pd, thereby enhancing Pd NPs' catalytic activity towards FA dehydrogenation.<sup>31</sup> To elucidate this possible electronic effect of the amine groups on Pd, Xray photoelectron spectroscopy (XPS) was employed to analyze the materials, and the results are displayed in Fig. 2, S2 and S3.<sup>†</sup> As seen in the spectra, while the peaks corresponding to Pd(0) in SBA-15/Pd with maxima are centered at 341.0 eV (3d<sub>3/2</sub> state) and 335.8 eV (3d<sub>5/2</sub> state),<sup>32</sup> the corresponding peaks in the case of SBA-15-Amine/Pd are shifted to lower binding energies of 340.1 eV and 335.0 eV, respectively. This is likely due to the interaction between Pd NPs and amine groups in SBA-15-Amine/Pd; i.e., the amine groups donate some electron density to Pd NPs and produce electron-rich Pd centers with lower binding energies. These electronically perturbed Pd centers in SBA-15-Amine/Pd could thus be responsible for the material's improved catalytic activity towards FA dehydrogenation compared with that



Scheme 1 A synthetic scheme showing the preparation of ultrasmall Pd nanoparticles supported on amine-functionalized SBA-15 mesoporous silica, which can efficiently catalyze formic acid (FA) dehydrogenation.



Fig. 1 TEM (a) and STEM (b) images of SBA-15-Amine/Pd. TEM (c) and STEM (d) images of SBA-15/Pd. The insets show the size distributions of the particles obtained from the TEM images.



Fig. 2 The high resolution  $\mathsf{Pd}_{3d}$  peaks in the XPS spectra of SBA-15-Amine/Pd and SBA-15/Pd.

of SBA-15/Pd (*vide infra*). It is worth adding here that the  $Pd_{3d}$  spectra of both materials showed two small peaks corresponding to  $Pd^{2+}$  centered at 343.2 eV and 337.9 eV, respectively, indicating the negligible presence of  $Pd^{2+}$  species.

Next, we evaluated the catalytic activities of SBA-15-Amine/ Pd, SBA-15-Amine, SBA-15/Pd, and bare Pd NPs toward FA dehydrogenation at room temperature in the absence of external bases using the set-up shown in Fig. S4.† As illustrated in Fig. 3, among these various materials we investigated, SBA-15-Amine/Pd showed superior activity towards FA dehydrogenation. The rate and amount of total H2-release from FA over SBA-15-Amine/Pd were quite good, with an initial TOF of 293  $h^{-1}$  in 10 min, which is among the highest TOFs for FA dehydrogenation previously reported for other heterogeneous catalysts under ambient conditions without bases.11-20 The TOFs of recently developed heterogeneous catalysts without additives at ambient temperature are compared in Table S1† entries 1–6 and Fig. S5.† It is also valuable to compare with a recently reported most active palladium catalyst, Pd/MSC-30, under ambient conditions that employed sodium formate along with formic acid in the reaction (Table S1,† entry 7).<sup>33</sup> The control materials, SBA-15/Pd and Pd NPs, showed only little catalytic activity, again supporting that the amine functional groups in SBA-15-Amine/ Pd play a pivotal role in accelerating FA dehydrogenation. It is also worth noting that the mesoporous silica material has no activity on its own towards the reaction.

To further scrutinize the potential roles of the covalently tethered amine functional groups in the catalytic activity of the material towards FA dehydrogenation, we carried out additional controlled experiments by using the physical mixtures of SBA-15/Pd and various quantities of *n*-propylamine (PA) as catalysts. Compared with SBA-15/Pd, the physical mixture of SBA-15/Pd and 0.1 mmol of PA showed an increased catalytic activity



Fig. 3 FA dehydrogenation catalyzed by the various materials synthesized and investigated here. (a) The volume of total gases produced *versus* time (min) curves. (b) TOFs at 10 min calculated based on the mol of Pd in the materials (catalysts). Reaction conditions: 10 mL of 1 M FA was stirred with 50 mg of a desired catalyst (16  $\mu$ mol of palladium) at room temperature at 300 rpm.

(Fig. 3a and b). Note that the amount of amine or PA added is 0.1 mmol, which is almost equal to that of covalently tethered amines in SBA-15-Amine/Pd. Upon addition of a higher amount (5 mmol) of PA (Fig. 3a, indicated with pink triangles), the corresponding activity increased slightly, but was still significantly lower than that obtained with SBA-15-Amine/Pd. Nevertheless, these results strongly imply that the added amine clearly acted as a Brønsted base, helping the deprotonation of FA. The results also suggest that the amine functional groups on the pore walls of SBA-15-Amine/Pd play multiple functions; *i.e.*, effectively deprotonating FA, besides facilitating the synthesis of well-dispersed, electron rich, and catalytically active ultrasmall Pd NPs for FA dehydrogenation. As a result, the rate of dehydrogenation of FA over SBA-15-Amine/Pd is much more enhanced.

FA is known to decompose *via* two possible pathways: (1) dehydrogenation (HCOOH  $\rightarrow$  H<sub>2</sub> + CO<sub>2</sub>) and dehydration (HCOOH  $\rightarrow$  H<sub>2</sub>O + CO).<sup>34</sup> To obtain better FA dehydrogenation systems for hydrogen production, catalysts that favor the former and suppress the latter are unquestionably preferred. This is

because the second (dehydration) process does not produce  $H_2$ , not to mention it forms CO – a common poison for many catalysts, including the Pt catalysts typically used in hydrogenfed PEMFCs.<sup>35-39</sup> To examine the selectivity of the overall reaction to the one leading to the desired product, *i.e.*,  $H_2$ , defined as [moles of  $H_2$ /moles of ( $H_2 + CO$ )] × 100, FT-IR spectroscopy was employed to detect CO directly (Fig. S6†). The FT-IR spectra obtained using SBA-15-Amine/Pd after 50 min gave a doublet peak located at *ca.* 2300 cm<sup>-1</sup>, indicating the evolution of CO<sub>2</sub>. The peak at *ca.* 2100 cm<sup>-1</sup> corresponding to CO was barely observable, strongly suggesting that the  $H_2$  selectivity is close to *ca.* 100%.

Recyclability studies of the catalytic material were additionally carried out for SBA-15-Amine/Pd. The result revealed that the catalyst was reusable at least six times without losing its activity (Fig. 4). Interestingly, the TOFs were, in fact, found to increase after the 1st run and become nearly identical for 2nd to 6th runs, reaching values as high as  $377 \text{ h}^{-1}$ . Consistent with these results, the TEM images of SBA-15-Amine/Pd revealed no appreciable change in the structure of mesoporous silica even following completion of the 6th catalytic recycle run. Moreover, the size of Pd NPs also remained unchanged (Fig. 5). The improved performance of the recycled catalysts particularly after the first cycle can be attributed to the reductive environment (due to the H<sub>2</sub> produced by the reaction) that the catalyst is exposed to during the catalytic reactions, which can convert any surfaceoxidized PdO (possibly present on the original catalyst) back to the catalytically active Pd NPs. The reduction condition can also prevent the Pd NPs from undergoing oxidation and losing their activity. Finally, to determine possible leaching of Pd from SBA-15-Amine/Pd during the reactions, the supernatant obtained after 150 min was examined by ICP-AES. The amount of Pd in the supernatant was found to be only ca. 10 ppm, indicating that the Pd NPs remain supported on SBA-15-Amine/Pd during the dehydrogenation reaction.



Fig. 4 Recyclability results of SBA-15-Amine/Pd used in FA dehydrogenation: volume (mL) of gas products ( $H_2 + CO_2$ ) versus time (min). The inset shows a plot of initial TOFs versus catalytic recycle runs.



Fig. 5 TEM images of spent SBA-15-Amine/Pd catalysts after each catalytic reaction cycle.

In addition, the amount of amine in the materials after the 6th recycle, obtained based on analysis of atomic percentage of nitrogen on XPS (Table S2 and Fig. S7†), remains almost unchanged.

In conclusion, amine-functionalized SBA-15-supported ultrasmall Pd NPs are synthesized and shown to have excellent activity towards FA dehydrogenation at room temperature in the absence of any external base, giving an initial TOF of 293  $h^{-1}$ , one of the highest values reported so far for heterogeneous catalysts, to the best of our knowledge (Table S1 and Fig. S5<sup>†</sup>). Despite the difference in synthetic strategies, the support materials, the metals involved and the catalytic procedures used in our case versus those in previously reported cases, based on the catalytic outcomes there appears to be the so-called strong metal-molecular support interaction (SMMSI) reported by Yadav et al.<sup>26</sup> at play in our material as well. This interaction, in turn, could also be partly responsible for the enhanced catalytic activities attained by the material. But some other subtle metalligand interactions may have also contributed to the higher catalytic activity in our case as compared with the non-ligand counterparts because: (1) the surface properties, the size of the metal-nanoparticles of the amine-grafted catalysts and nonamine catalysts like ours are quite different and (2) based on recently reported mechanistic details<sup>31</sup> as well as some of our ongoing work, we also believe that the supported amine groups play an additional role as a base.

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