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## COMMUNICATION



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# **dehydrogenation of formic acid**<sup>+</sup> Hongmei Dai,<sup>a</sup> Nan Cao,<sup>a</sup> Lan Yang,<sup>a</sup> Jun Su,<sup>c</sup> Wei Luo<sup>\*ab</sup> and Gongzhen Cheng<sup>a</sup>

AgPd nanoparticles supported on MIL-101 as high

performance catalysts for catalytic

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Bimetallic AgPd nanoparticles were successfully immobilized into the metal-organic frameworks (MIL-101), and tested for their catalytic dehydrogenation of formic acid. These catalysts were composition dependent for the catalytic activity. Among all the AgPd@MIL-101 catalysts tested, the Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 catalyst exhibits the highest catalytic activity for the conversion of formic acid to high-quality hydrogen at 80 °C with a TOF value of 848 h<sup>-1</sup>, which is among the highest values reported at 80 °C.

Hydrogen, producing only water as a byproduct, has been considered the most promising solution for alternative energy applications.1 However, one of the most important application obstacle is the safe and efficient storage of hydrogen.<sup>2</sup> Various hydrogen storage approaches are currently being investigated, including metal hydrides,3 sorbent materials,4 and chemical hydride systems.<sup>5</sup> Among them, formic acid, as a major product of biomass processing with high hydrogen content (4.4 wt%), high stability, environmental benignity, and easy recharging ability, has been identified as a safe and convenient hydrogen carrier for portable hydrogen storage application.6 Moreover, formic acid is a liquid-phase material which has the potential to accept the existing liquid-based distribution infrastructure, which makes formic acid more competitive compared with solid chemical hydrogen materials such as sodium borohydride (NaBH<sub>4</sub>) and ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) derivatives. Hydrogen stored in formic acid could be released via a complete decomposition method (eqn (1)), making CO<sub>2</sub> as the only by-product.<sup>7,8</sup> However, from the perspective of hydrogen storage application, the undesired reaction pathway (eqn (2)) should be avoided.<sup>9</sup>

 $\text{HCOOH(l)} \rightarrow \text{CO}_2(g) + \text{H}_2(g), \Delta G_{298} = -48.8 \text{ kJ mol}^{-1}$  (1)

HCOOH(l) → H<sub>2</sub>O(l) + CO(g), 
$$\Delta G_{298} = -28.5 \text{ kJ mol}^{-1}$$
 (2)

Recently, selective dehydrogenation of formic acid was observed with soluble catalysts of organometallic complexes<sup>10</sup> and some insoluble catalysts of noble metals deposited on different supports such as metal oxides and activated carbons.<sup>11</sup> However, finding the optimal balance state between cost, selectivity, efficiency and recyclability still remains a considerable challenge.

On the other hand, due to the high specific surface area and tunable pore size, metal–organic frameworks (MOFs) have attracted growing attention in the application of gas sorption and storage,<sup>12</sup> drug delivery,<sup>13</sup> and molecular separation.<sup>14</sup> Given the similarity to zeolites, loading of metal nanoparticles (NPs) inside the porous materials of MOFs could afford solid catalysts. The porous structures of MOFs could restrain the aggregation of the metal NPs, and further affect the catalytic activity and recyclability of the catalysts. Loading of metal NPs into the porous structures of MOFs is of current interest.<sup>15,16</sup>

It has been reported that bimetallic NPs can promote the catalytic activity and selectivity of the monometallic species. In recent years, Ag–Pd bimetallic NPs including AgPd alloy, Ag–Pd core–shell, and monodisperse AgPd alloy NPs supported on carbon based materials have been developed for catalytic dehydrogenation of formic acid.<sup>17–21</sup> However, to the best of our knowledge, there is currently no report about using Ag–Pd alloy NPs supported on MOFs as catalysts for the dehydrogenation of formic acid. Herein, we report, for the first time, the generation of highly dispersed AgPd NPs immobilized in MIL-101 as a highly efficient catalyst for dehydrogenation of formic acid. Compared with other reported catalysts, the  $Ag_{20}Pd_{80}$ @MIL-101 catalyst exhibits the highest activity with a TOF value of 848 h<sup>-1</sup> at 80 °C, and 100% selectivity for hydrogen generation from formic acid solution.

MIL-101 with two cavities of *ca.* 2.9 and 3.4 nm free diameters accessible through two pore windows of *ca.* 1.2 and 1.6 nm

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#### Communication

was chosen because of its extra high specific surface area, high thermal stability (up to 300 °C), and high chemical stability in water.22 MIL-101 was synthesized according to the literature.23 The un-reacted terephthalic acid in the pores were removed by solvothermally treating with ethanol and aqueous NH<sub>4</sub>F solution, respectively. The supported AgPd@MIL-101 catalyst was prepared through solution infiltration of activated MIL-101 with  $H_2PdCl_4$  and AgNO<sub>3</sub> at pH = 3.0, followed by treatment with NaBH<sub>4</sub>. The low-angle powder X-ray diffractions (PXRD) of the as-synthesized MIL-101, activated MIL-101, Pd@MIL-101, Ag@MIL-101, and Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 exhibit no loss of crystallinity (Fig. 1a), indicating that the integrity of the MIL-101 framework was maintained well during the catalyst preparation. Furthermore, the wide-angle PXRD pattern of Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 (Fig. 1b) exhibited a broad peak between the characteristic peaks for Ag(111) and Pd(111), indicating the formation of the Ag-Pd alloy. The morphologies of MIL-101 immobilized Ag20Pd80 NPs were further characterized by transmission electron microscopy (TEM) (Fig. 2) and energy-dispersive X-ray spectroscopy (EDX) measurements (Fig. S1<sup>†</sup>). The EDX spectra confirm the presence of Ag-Pd. TEM images of AgPd@MIL-101 indicate that the AgPd NPs are well dispersed, and encapsulated in the cages of the MIL-101. The mean diameter of AgPd NPs in AgPd@MIL-101 was in the range of 2.7  $\pm$  0.2 nm (Fig. S2<sup>†</sup>), which are small enough to be immobilized into the mesoporous cavities of MIL-101 (2.9 and 3.4 nm), and big enough to be limited in the pores of the framework by the windows of MIL-101 (1.2 and 1.6 nm), resulting in the high catalytic activity and durability for dehydrogenation of formic acid (vide infra). A representative high-resolution TEM image in Fig. 2a shows a dspacing of 0.232 nm, which is between the (111) lattice spacing of face-centered cubic (fcc) Ag (0.24 nm) and fcc Pd (0.22 nm), further suggesting that AgPd is formed as an alloy structure. The N<sub>2</sub> adsorption-desorption isotherms of MIL-101 and Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 are shown in Fig. 3. The specific areas of MIL-101 and  $Ag_{20}Pd_{80}$  (MIL-101 were 2232.80 and 1111.02 m<sup>2</sup> g<sup>-1</sup> respectively.<sup>24</sup> The large decrease in the amount of N<sub>2</sub> adsorption and the pore volume<sup>25</sup>(Fig. S3 and Table S1<sup>†</sup>) of Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 indicates that the cavities of MIL-101 were either occupied or blocked by the well dispersed AgPd NPs. In the X-ray



Fig. 2 (a and b) TEM images of  $Ag_{20}Pd_{80}$ @MIL-101 reduced by sodium borohydride; (c and d) TEM images of  $Ag_{20}Pd_{80}$ @MIL-101 after five runs of catalytic hydrolysis of HCOOH.



Fig. 3  $N_2$  sorption isotherms of (a) activated MIL-101; (b)  $Ag_{20}Pd_{80}@MIL-101$  at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively.



Fig. 1 [a and b] Low-angle and wide-angle powder X-ray diffraction patterns of samples: (a) MIL-101; (b) activated MIL-101; (c) Pd@MIL-101; (d)  $Ag_{20}Pd_{80}@MIL-101$ ; (e)  $Ag_{20}Pd_{80}@MIL-101$ ; (e)  $Ag_{20}Pd_{80}@MIL-101$  after five runs of catalytic hydrolysis of HCOOH; (f) Ag@MIL-101. The characteristic peak of Pd(111) is at  $2\theta = 40.1^{\circ}$ , the characteristic peak of Ag(111) is at  $2\theta = 38.03^{\circ}$ .



Fig. 4 Hydrogen generation from HCOOH in the presence of different catalysts:  $Ag_{20}Pd_{80}$ @MIL-101;  $Ag_{35}Pd_{65}$ @MIL-101;  $Ag_{48}Pd_{52}$ @MIL-101;  $Ag_{63}Pd_{37}$ @MIL-101;  $Ag_{78}Pd_{22}$ @MIL-101; Ag@MIL-101; Pd@MIL-101 at 80°.

photoelectron spectroscopy (XPS) (Fig. S4<sup>†</sup>), the  $3d^{5/2}$  and  $3d^{3/2}$  peaks of Pd<sup>0</sup> at 335.2 and 340.5 eV,<sup>26</sup> and the  $3d^{5/2}$  and  $3d^{3/2}$  peaks of Ag<sup>0</sup> at 374.3 and 340.5 eV (ref. 27) were observed, indicating the co-existence of both metals.

The composition of the AgPd NPs was tuned by the initial molar ratio of H<sub>2</sub>PdCl<sub>4</sub> and AgNO<sub>3</sub> and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Table S2<sup>†</sup>). Ag@MIL-101, Ag<sub>78</sub>Pd<sub>22</sub>@MIL-101, Ag<sub>63</sub>Pd<sub>37</sub>@MIL-101, Ag<sub>48</sub>Pd<sub>52</sub>@MIL-101, Ag<sub>35</sub>Pd<sub>65</sub>@MIL-101, Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101, and Pd@MIL-101were synthesized using metal precursors at the Ag/Pd ratios of 5:0, 4:1, 3:2, 1:1, 2:3, 1:4, and 0:5, respectively. The catalytic dehydrogenation of formic acid has been performed over all the samples at 80 °C in the presence of sodium formate as shown in Fig. 4. The catalytic activity was strongly dependent on the Ag-Pd composition, while Ag@MIL-101 was catalytically inactive. Among all the bimetallic AgPd@MIL-101 catalysts investigated, Ag20Pd80@MIL-101 exhibited the highest catalytic activity, with a turnover frequency (TOF) value of 848  $\text{mol}_{H_2} \text{ mol}_{\text{metal}}^{-1} \text{ h}^{-1}$  at 80 °C, which is the highest among all the previously reported catalysts (Table 1). Moreover, 140 mg of formic acid can be completely converted into H<sub>2</sub> and CO<sub>2</sub> in 15 min only in the presence of 100 mg of the Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 catalyst, while other MIL-101 supported bimetallic AgPd NPs resulted in incomplete dehydrogenation of formic acid. These results further indicate the molecular-scale synergy of Ag-Pd alloy NPs. In addition, as a control experiment, the same amount of Ag20Pd80 NPs and MIL-101 were synthesized and applied to the same reaction (Fig. S5<sup>†</sup>). Almost no reactivity was observed for MIL-101, and less than 30 mL gas was generated over 20 min for Ag<sub>20</sub>Pd<sub>80</sub> NPs, indicating the synergetic effect of Ag-Pd alloy NPs and MIL-101. By selectively removing  $CO_2$ , the gas released during the reaction was passed through a trap containing 5 M NaOH solution to ensure the complete absorption of  $CO_2$  (Fig. S6<sup>†</sup>). The volume of gas passed through NaOH solution was reduced to half, indicating generation of hydrogen and carbon dioxide completely, with no evidence of CO. Furthermore, only CO<sub>2</sub> but no CO has been detected by gas chromatography (GC) analyses (Fig. S7<sup>†</sup>),<sup>28</sup> indicating the excellent H<sub>2</sub> selectivity for formic acid

Table 1	Catalytic activity of catalysts for catalytic hydrolysis of formic
acid	

Catalyst	Temp (°C)	${\mathop{\rm TOF}\limits_{\left(h^{-1} ight)}}$	Activation energy (kJ mol <sup>-1</sup> )	Ref.
Ag <sub>20</sub> Pd <sub>80</sub> @MIL-101	80	848	27	This
				work
AuPd@ED-MIL-101	90	106		16
Pd-S-SiO <sub>2</sub>	85	719		29
PdAu@Au/C	92	21.4		30
PdAu/C-CeO <sub>2</sub>	92	113.5		31
Co <sub>0.30</sub> Au <sub>0.35</sub> Pd <sub>0.35</sub>	25	80		32
$Ag_{48}Pd_{52}$	50	382	22	21
Au/C	50	80		33
Ag/Pd alloy	20	144		18
Ag@Pd/C	20	192		18
Pd/C with citric acid	25	64		34
PdNi@Pd/GN <sub>s</sub> -CB	25	577		8
Pd-Au-Dy/C	92	269	98.3	35
Pd–Au-Ho/C	92	224	102.1	35
Pd-Au/C	92	45	138.6	35

dehydrogenation by the Ag20Pd80@MIL-101 catalyst. Furthermore, as a control experiment, the same amount of Ag<sub>20</sub>Pd<sub>80</sub> NPs and MIL-101 was synthesized and applied to dehydrogenation of formic acid. As shown in Fig. S8,† for Ag<sub>20</sub>Pd<sub>80</sub>, less than 40 mL gas was released over 20 min, and almost no reactivity was observed for MIL-101 toward hydrogen generation from formic acid and sodium formate solution at 80 °C. These results confirm the synergetic effect of AgPd NPs and the framework of MIL-101. To get the activation energy  $(E_a)$  of the dehydrogenation of formic acid catalyzed by Ag20Pd80@MIL-101, the reactions at different temperatures in the range of 50-80 °C were carried out. The values of rate constant k at different temperatures were calculated from the slope of the linear part of each plot from Fig. 5a. The Arrhenius plot of  $\ln k vs. 1/T$  for the catalyst is plotted in Fig. 5b, from which the apparent activation energy was determined to be approximately 27.04 kJ mol<sup>-1</sup>, being lower than most of the reported values. The durability is important for the application of catalysts. We tested the durability of the Ag20Pd80@MIL-101 catalyst in the decomposition of formic acid at 80 °C. Subsequent addition of the same amount of formic acid after the completion of the previous run resulted in no significant decrease in catalytic activity and no change in the hydrogen selectivity even after the fifth run (Fig. S8†). Fig. 2c and d show a representative TEM image of Ag20Pd80@MIL-101 NPs after the fifth run durability test. As clearly seen from the TEM image, there is no noticeable change. Furthermore, from the PXRD in Fig. 1, it is observed that the integrity of the MIL-101 framework is maintained well during the catalyst test after the fifth run.

In summary, we have developed a facile method for immobilizing ultrafine AgPd alloy NPs into the frameworks of MIL-101. These catalysts were composition dependent toward dehydrogenation of formic acid at 80 °C. The Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 catalyst exhibits a marked superiority over its monometallic and bimetallic counterparts with different ratios, indicating a strong molecular-scale synergy of Ag–Pd alloy. Moreover, the Ag<sub>20</sub>Pd<sub>80</sub>@MIL-101 catalyst exhibits superior catalytic activity





and selectivity than  $Ag_{20}Pd_{80}$  NPs without any support, and MIL-101 without metal NPs, suggesting the synergetic effect of AgPd NPs and the framework of MIL-101. The combination of high activity and selectivity as well as good durability enables AgPd@MIL-101 to act as a potential catalyst for practical application in dehydrogenation of formic acid for chemical hydrogen storage. Furthermore, this simple synthetic method can be extended to other water stable MOFs as effective supports to immobilize bimetallic/polymetallic metal NPs for more applications.

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