Amine-Functionalized MIL-125 with Imbedded Palladium Nanoparticles as an Efficient Catalyst for Dehydrogenation of Formic Acid at Ambient Temperature

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ABSTRACT: Palladium nanoparticles were immobilized within the pores of metal organic frameworks MIL-125 and amine-functionalized NH2-MIL-125 using photoassisted and ion exchange deposition methods. The resulting materials showed a very high activity for hydrogen production at ambient temperature in comparison to other titanium-based porous materials. The amine groups in NH2-MIL-125 greatly increased the H2-generating activity and acted as a stabilizer of Pd NPs. The photoassisted deposition method was a more efficient method for producing highly dispersed small NPs in the MOF materials.

1. INTRODUCTION

Hydrogen (H2), an excellent compact energy carrier, has a potential to replace fossil fuels in the future, but first, problems with the storage and production must be resolved.1–4 A feasible option is to store H2 in an organic liquid medium, which can release H2 in situ at ambient temperature for direct use in fuel cells. Formic acid (FA) is considered a convenient H2 carrier because it is a liquid at room temperature, nontoxic, and contains 4.4 wt % (53 g/L) of H2.5 The decomposition of FA can follow two pathways

\[ \text{dehydrogenation: } HCOOH \leftrightarrow H_2 + CO_2 \]
\[ \Delta G = -48.4 \text{ kJ/mol} \] (1)

and

\[ \text{dehydration: } HCOOH \leftrightarrow CO + H_2O \]
\[ \Delta G = -28.5 \text{ kJ/mol} \] (2)

The first pathway is regarded as a promising H2-generating process, but the second is not desirable because CO is toxic to fuel cell catalysts and a concentration below 10 ppm CO gas is highly desirable.6

Recently, the selective dehydrogenation of FA in homogeneous reactions with organometallic complexes7,8 heterogeneous reactions with noble metal nanoparticles (NPs),9 and on solid supports10–13 has been reported. Yet, only few reports have demonstrated the dehydrogenation reaction at ambient temperature using a heterogeneous catalyst9,14 which is necessary for practical application (for example, in fuel cells). Thus, it is highly desirable to develop a high-performance heterogeneous catalyst capable of H2 generation from FA at ambient temperature.

Metal organic frameworks (MOFs), also called porous coordination polymers (PCPs), are an attractive class of porous organic–inorganic crystalline materials15–18 and have found use for applications in catalysis,19,20 as membranes,21 optical materials,22 carbon dioxide capture,23 and H2 storage.24 They are built from connecting metal ions to organic linkers to form uniform pore sizes and volumes.25 The connecting organic linkers give a greater chemical diversity because they can be modified by functional groups, which change the physiochemical properties.5,6,27 The functionalization of the organic linkers has essentially been used to increase the gas adsorption and stabilize the metal NPs,13,31 and their utilization in catalysis has not been explored.

Supported metal NPs are widely used in catalysis,32 and increasing efforts have been made to prepare small and well-dispersed NPs inside of MOF materials. A recent review by Moon et al. summarized different methods of preparation of metal NPs within MOF materials.33 Currently, there are no reports studying the impact of functionalized-MOF-immobilized metal NPs on heterogeneous catalysis, although a higher...
catalytic activity attained by metal NPs on porous materials with grafted functional groups was shown previously.34−37

Herein, we describe a preparation of Pd NPs within the titanium-based MOF MIL-12538 and NH2-MIL-125,39 and carry dehydrogenation of FA at ambient temperatures. We demonstrate that Pd NPs embedded in the material with the functional groups display higher catalytic activity at ambient temperature owing to the amine functional groups. MIL-125 type was chosen as a support because it has large pore and window sizes that can facilitate NPs and contains photoactive Ti ions. To our knowledge, there are no reports of FA dehydrogenation at ambient temperature using functionalized-MOF-immobilized metal NPs and nonfunctionalized-MOF-immobilized metal NPs and comparing their catalytic performance.

2. EXPERIMENTAL SECTION

Catalysts Preparation. MIL-125 was prepared using a method published by Ferey38 in which 1,4-benzene dicarboxylic acid (15 mmol, Nacalai Tesque, 99.5%) and titanium isopropoxide (9 mmol, Nacalai Tesque, 99.8%) were added into a 50 mL solution containing N,N-dimethylformamide (DMF, Nacalai Tesque, 99.8%) and methanol (CH3OH, Nacalai Tesque, 99.8%) in a 9:1 ratio. The mixture was stirred at ambient temperature, transferred to 50 mL Teflon-lined stainless steel autoclaves, and heated 16 h at 423 K. After the reaction, the product of the synthesis was extracted by centrifugation and washed with DMF and methanol, respectively. The obtained white solid was dried under vacuum and activated by calcination for 6 h at 473 K. A modified procedure was used for the preparation of the NH2-functionalyzed MIL-125. Titanium isopropoxide (3.5 mmol) and 2-amino benzene dicarboxylic acid (7.0 mmol, TCI, 98%) were added to 50 mL of a DMF and CH3OH (1:1) solution and heated in Teflon-lined stainless steel autoclaves for 16 h at 423 K. The identical procedure was used for the product recovery and activation.

The Pd NP deposition was carried out with the intention to obtain 0.5 wt % concentrations. Pd NPs were introduced into MIL-125 and NH2-MIL-125 by an aqueous photoassisted deposition method; 200 mg of powdered sample was suspended in 20 mL of distilled water and activated by ultrasound inside of a quartz vessel for 30 min. Then, 0.8 mL of aqueous solution PdCl2 (11.64 mM, TCI, 98%) was added, and the suspension was stirred at ambient temperature for 10 h. The resulting material was recovered by centrifugation, washed with H2O, and dried under vacuum. The dried powder was then reduced in H2 at 473 K for 4 h. The sample is denoted as Pd-NH2-MIL-125.

Characterization. X-ray powder diffraction patterns were recorded using a Rigaku RINT2500 diffractometer with Cu Kα radiation (λ = 1.5406 Å). Infrared spectra were collected on a JASCO FTIR-6100. Samples were diluted with KBr and compressed into thin disk-shaped pellets. Reflectance UV spectra of powdered samples were collected using a Shimadzu UV-2600 photospectrometer. The reference was BaSO4, and the absorption spectra were obtained using the Kubelka–Munk function. BET surface measurements were performed using a BELSORP-max system (BEL Japan, Inc.) at 77 K. Samples were degassed under vacuum at 473 K for 24 h prior to data collection. Transmission electron microscopy (TEM) images were obtained using a Hitachi H-800 electron microscope equipped with an energy-dispersive X-ray (EDX) detector, operated at 200 kV. Pd K-edge XAFS spectra were recorded at the beamline BL01B1 station at SPring-8 equipped with a Si(311) monochromator, JASRI, Harima, Japan. The 8 GeV electron storage ring was operated in a top-up mode with an injection period of 1 min. The stored beam current was 70 mA (±0.1%). The data were collected in a fluorescence mode using a 19-element solid-state detector. The raw XAFS data obtained were processed by REX2000. Normalization and background subtraction of the data were carried out using the Athena software package.40,41 The AUTOBK method was used to isolate the k-space EXAFS data from the raw data.

Dehydrogenation of FA. A powdered sample (50 mg) and 5 mL of H2O were added to a Pyrex reaction vessel (30 cm3), sealed with a rubber septum, and bubbled with argon gas for 30 min. Then, a solution containing 4.6 mL of H2O, 0.39 mL of HCOOH, and 0.54 g of HCOONa was injected to the Pyrex reaction vessel. The reaction vessel was then placed in an oil bath at 305 K with magnetic stirring for 3 h. The progress of the reaction was monitored by a Shimadzu GC14B equipped with an MS S column (H2) and Shimadzu GC (CO2).
3. RESULTS AND DISCUSSION

The as-prepared materials MIL-125 and NH2-MIL-125 were highly crystallized with matching XRD patterns (Figure 1). A considerable decrease in BET surface area for NH2-MIL-125 was caused by the presence of amine groups inside of the cavities. The presence of the NH2 groups in the organic likers has been confirmed on evacuated samples by IR spectroscopy (Figure S1 (Supporting Information) displays the FTIR spectra of the evacuated samples MIL-125 and NH2-MIL-125, and Figure S2 shows the spectra of 1,4-benzene dicarboxylic acid and 2-amino benzene dicarboxylic acid). The octahedral coordination of titanium species in MIL-125 was confirmed by UV−vis (Figure 1) as a broad absorption edge to 350 nm. NH2-MIL-125 displays an additional absorption edge in the visible region, induced by O to Ti charge transfer (ligand to metal charge transfer) in the TiO5(OH) inorganic cluster.39

The BET surface area of MIL-125 was 1443 m2 g−1 with a pore volume of 0.68 cm3 g−1, and a considerable decrease to 1270 m2g−1 and a 0.63 cm3 g−1 pore volume for NH2-MIL-125 was due to the presence of the amine group in the ligand (Figure 1 inset and Table 1).

Table 1. BET Surface Area and Pore Volume of MIL-125 and NH2-MIL-125 with Pd NPs Obtained from N2 Adsorption−Desorption Isotherm Measurements

<table>
<thead>
<tr>
<th>sample</th>
<th>BET (m2 cm−1)</th>
<th>pore volume (cm3 g−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-125</td>
<td>1443</td>
<td>0.68</td>
</tr>
<tr>
<td>NH2-MIL-125</td>
<td>1270</td>
<td>0.63</td>
</tr>
<tr>
<td>Pd-MIL-125</td>
<td>1103</td>
<td>0.62</td>
</tr>
<tr>
<td>Pd-NH2-MIL-125</td>
<td>1179</td>
<td>0.57</td>
</tr>
<tr>
<td>Pd-NH2-MIL-125i</td>
<td>948</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Figure 1 displays the XRD patterns and BET surface area plots of the samples after the photoassisted and ion-exchanged immobilization of 0.5 wt % Pd NPs. There was no visible loss in homogeneity and crystallinity in the XRD, suggesting that the integrity of the framework was preserved. The characteristic Pd(111) peak was not detected because of the low intentional Pd loadings (0.5 wt %). A significant decrease in the BET surface area and pore volume (Table 1) indicates that the internal cavities were occupied or blocked by Pd NPs. The NH2-MIL-125i prepared by the ion exchange method showed a larger decrease in BET in comparison with NH2-MIL-125 prepared by the photoassisted deposition method, implying a smaller size and dispersion of the metal NPs.

X-ray absorption measurements (XAFS) were carried out to elucidate the electronic structure and chemical environment of the Pd NPs. Figure 3A shows the normalized X-ray absorption near-edge structure (XANES) spectra at the Pd K-edge for Pd foil, Pd-MIL-125, Pd-NH2-MIL-125, and Pd-NH2-MIL-125i. The XANES depends on the electronic state of the central atom. The Pd foil XANES display two distinct peaks at 24364 and 24386 eV due to 1s → 5p transition. The shapes of the XANES spectra for supported Pd NPs resemble those of the Pd foil, suggesting the presence of the Pd(0) in the samples. Figure 3B shows the Fourier transforms (FTs) k3-weighted Pd K-edge extended X-ray absorption fine structure (EXAFS) of these samples. The Pd foil displays a main peak centered at 2.65 Å, which is assigned to a single Pd–Pd bond in a metallic form. Similarly, the Pd species within the MOF materials also exhibit the single peak centered at 2.65 Å, corresponding to the Pd–Pd metallic bond. The intensity of the FT has been used to obtain information about the coordination number, and the FT intensity increased in the following order: Pd-NH2-MIL-125 > Pd-MIL-125 > Pd-NH2-MIL-125i; thus, it can be assumed that the size of the Pd NPs is increasing in the same order.

Figure 4 displays TEM images of the Pd NPs immobilized within the pores of the MOF materials. Pd NPs formed within the Pd-MIL-125 have a mean diameter of 5.5 nm and narrow...
size distribution. Well-distributed and small NPs are formed within NH$_2$-MIL-125 with a mean diameter of 3.1 nm, prepared by the photoassisted deposition method, but larger NPs with a mean size of 5.6 nm are formed during the ion exchange. Clearly, the preparation method affects the size and dispersion of NPs, and the photoassisted methods give the best results in terms of controlling the dispersion and size of NPs.

To investigate factors such as the preparation method and the effect of the amine functional groups on the catalytic performance, dehydrogenation of FA was performed at ambient temperature. The reaction was carried out under an Ar atmosphere at 305 K in an oil bath, and the performance was compared to Pd NPs on other Ti-containing porous support materials, namely, TS-1 and Ti-MCM-41. Figure 5 shows the H$_2$ production from Pd NPs on different supports and the time course of the H$_2$ production for the MOF materials. Every Pd NP-supported material exhibited some H$_2$-producing activity, but no catalytic activity was observed in the control experiment with only pure support materials. Pd-TS-1 (Ti/Si = 57.7, photoassisted deposition method, 0.5 wt % Pd) and Pd–Ti-MCM-41 (5 mol % Ti, photoassisted deposition method, 0.5 wt % Pd) were the least efficient catalysts, generating only 1.7 and 5.1 μmol of H$_2$, respectively. Pd-NH$_2$-MIL-125 displayed the best catalytic performance, generating 48.1 μmol; Pd-NH$_2$-MIL-125i produced 43.1 μmol, and Pd-MIL-125 produced only 17.8 μmol. The ratio of H$_2$ and CO$_2$ generated during the reaction was approximately 1. The CO concentration during the dehydration reaction for Pd-NH$_2$-MIL-125 never exceeded 5 ppm. While the H$_2$ generation by Pd-MIL-125 nearly ceased after 1 h, the Pd-NH$_2$-MIL-125 continued to generate H$_2$ at a nearly linear rate after the initial period, but the H$_2$ production decreased for Pd-NH$_2$-MIL-125i. The catalyst can be reused after the reaction because the structure of the catalysts is preserved (Figure S4, Supporting Information). Leaching of the active components into the reaction solution was not confirmed because the reaction carried out with only the separated solution did not generate any H$_2$ gas.

The turnover frequency (TOF) of the best-performing catalyst was 214 h$^{-1}$ for the Pd-NH$_2$-MIL-125 catalyst working...
at 305 K, which is much higher than that for the Ag@Pd/C (49 h\(^{-1}\), 313 K), \(^{43}\) Au/Al\(_2\)O\(_3\) (64 h\(^{-1}\), 313 K), and Pd–Au/C (27 h\(^{-1}\), 365 K). \(^{42}\) Furthermore, the catalytic system presented here is capable of generation of H\(_2\) without the unfavorable formation of CO (less than 5 ppm). The catalyst keeps almost its original activity after the recycling experiments.

From these results, it is clear that the average size of Pd NPs is not the most important factor in attaining the high catalytic activity; essentially, it is caused by the amine functional groups. The amine groups in MOFs are known to prevent agglomeration of metal NPs,\(^{43}\) and the presence of amine has also been reported to increase the catalytic activity for FA decomposition in other systems.\(^{14,44}\) However, the increased catalytic performance at ambient temperature for FA decomposition by the −NH\(_2\) functional groups within the nanoporous structure of the MOF has been observed for the first time. The reaction mechanism can be deduced from a mechanism for FA decomposition with Pd NPs supported on basic resin.\(^{45}\) Here, the reaction intermediate are Pd-formate species, and the weakly basic −NH\(_2\) group acts as a proton scavenger, forming −HNH\(_2\). Pd-formate species then undergo \(\beta\)-hydride elimination to produce CO\(_2\) and a Pd hydride species. The basic −NH\(_2\) groups within the MOF have a positive effect on the O–H bond dissociation, and the cooperation of the amine functionality within the MOF structure and NPs is responsible for the high catalytic activity.

4. CONCLUSION

In summary, we used a photocatalytically active MOF MIL-125 and its amine-functionalized equivalent NH\(_2\)-MIL-125 to immobilize Pd NPs by photoassisted and ion exchange deposition methods. The Pd NPs embedded within the amine-functionalized NH\(_2\)-MIL-125 showed high catalytic activity for H\(_2\) generation from FA at ambient temperature in comparison to MIL-125. The main factors responsible for the high catalytic performance were the basic functionalization of the MOF and small NP size. The photoassisted deposition method was a more effective method for producing small and highly dispersed NPs within the MOF structure. The amine-functionalized NH\(_2\)-MIL-125 is beneficial for an increased durability of the MOF in an aqueous environment. The present work shows that functionalization can greatly enhance the catalytic performance of MOF materials and can be extended to other metal NPs and functional groups in MOFs.

ASSOCIATED CONTENT

Supporting Information

FTIR spectra of MIL-125, NH\(_2\)-MIL-125, 1,4-benzene dicarboxylic acid, and 2-aminobenzenedicarboxylic acid, the TEM image of Pd-NH\(_2\)-MIL-125, and XRD patterns of NH\(_2\)-MIL-125 and MIL-125. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES


