Synergistic Catalysis of Metal–Organic Framework-Immobilized Au–Pd Nanoparticles in Dehydrogenation of Formic Acid for Chemical Hydrogen Storage

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§Supporting Information

ABSTRACT: Bimetallic Au–Pd nanoparticles (NPs) were successfully immobilized in the metal–organic frameworks (MOFs) MIL-101 and ethylenediamine (ED)-grafted MIL-101 (ED-MIL-101) using a simple liquid impregnation method. The resulting composites, Au–Pd/MIL-101 and Au–Pd/ED-MIL-101, represent the first highly active MOF-immobilized metal catalysts for the complete conversion of formic acid to high-quality hydrogen at a convenient temperature for chemical hydrogen storage. Au–Pd NPs with strong bimetallic synergistic effects have a much higher catalytic activity and a higher tolerance with respect to CO poisoning than monometallic Au and Pd counterparts.

The search for safe and efficient hydrogen storage materials remains one of the most difficult challenges for the transformation to a hydrogen-powered society as a long-term solution to current energy problems.‡ Formic acid, which is one of the major products formed in biomass processing and has an energy content at least 5 times higher than that of commercially available lithium ion batteries, represents a convenient hydrogen carrier in fuel cells designed for portable use. In general, formic acid can be decomposed via dehydrogenation (HCOOH → H2 + CO2) and dehydration (HCOOH → H2O + CO) pathways. For the subsequent conversion of hydrogen into electrical energy, the latter pathway producing the CO impurity, which is toxic to fuel cell catalysts, should be avoided.‡ Recently, selective dehydrogenation of formic acid was observed with soluble catalysts of organometallic complexes,§ and some insoluble catalysts of noble metals deposited on different supports such as metal oxides and activated carbons exhibit catalytic selectivity and activity.‡ For practical applications such as fixed-bed flow-through operations, the development of high-performance heterogeneous catalysts for hydrogen generation from formic acid is of great importance.

Porous metal–organic frameworks (MOFs) have emerged as a class of very promising hybrid functional materials.‡,§ Over the past decades, research efforts have been mostly aimed at preparing new MOF structures and studying their applications in molecule storage and separations.§ Because of the high surface area, porosity, and chemical tunability of MOFs, their logical application, especially when metal nanoparticles (NPs) are embedded into their pores, could be for solid-state catalysis.‡ To date, there have been a limited number of works on MOF-supported metal NPs and only one report of MOF-supported bimetallic alloy NPs with full characterization as catalysts for heterogeneous reactions.‡ More recently, we reported a route to the synthesis of core–shell and alloy NPs using ZIF-8 as a support and their catalytic performance in the reduction of 4-nitrophenol in water.‡ To the best of our knowledge, there are currently no reports of MOF-immobilized metal NPs with catalytic activity in the dehydrogenation of liquid-phase chemical hydrogen storage materials such as formic acid.‡

Herein we report the generation of hydrogen from formic acid over bimetallic Au–Pd NPs immobilized in mesoporous MOFs as efficient catalysts. MIL-101 was chosen as a support because of its large pore sizes (2.9–3.4 nm) and window sizes (1.2–1.4 nm) and its hybrid pore surface,§ which may facilitate the encapsulation of metal NPs and the adsorption of the catalytic substrate formic acid inside the pores. In order to improve the interactions between the metal precursors and the MIL-101 support, we grafted the electron-rich functional group ethylenediamine (ED) into MIL-101, which contains coordinatively unsaturated Cr3+ centers, to form ED-MIL-101,‡ which exhibited improved immobilization of small metal NPs.

Activated ED-MIL-101 (100 mg) was impregnated with deionized water (5 mL) containing HAuCl4 (50 mg) and H2PdCl4 (50 mg) at 35 °C for 24 h, and then the as-synthesized sample was treated in a stream of 1:1 H2/He at 200 °C for 3 h to yield Au–Pd/ED-MIL-101.‡ There was no apparent loss of crystallinity in the powder X-ray diffraction (PXRD) patterns after H2 reduction in Au–Pd/ED-MIL-101 with a loading of 20.4 wt % Au–Pd NPs (Au:Pd = 2.46),‡ suggesting that the integrity of the MIL-101 framework was maintained. The PXRD pattern of Au–Pd/ED-MIL-101 exhibited a broad peak between the characteristic peaks for Au(111) and Pd(111), indicating the formation of the Au–Pd alloy.‡ The appreciable decrease in the amount of N2 adsorption and the pore size of Au–Pd/ED-MIL-101 indicates that the cavities of the host framework are occupied by dispersed Au–Pd NPs and/or blocked by the Au–Pd NPs located at the surface (Figure 1), as in the case of metal NPs loaded into ZIF-8, MOF-5, and other porous materials.‡ The X-ray photoelectron spectrometry (XPS) investigation of Au–Pd/ED-MIL-101 at the Au 4f and Pd 3d levels exhibited metallic Au and Pd peaks that retained their intensity ratios during the Ar etching, indicating the homogeneity of the Au–Pd alloy particles.‡
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The obtained Au–Pd/ED-MIL-101 sample exhibited high catalytic activity in hydrogen generation from formic acid. This is the first example of a highly active porous-MOF-supported metal NP catalyst for hydrogen generation from a chemical hydrogen storage material at a convenient temperature. At 90 °C, 140 mg of formic acid can be completely converted to H₂ and CO₂ in 65 min in the presence of 20 mg of Au–Pd/ED-MIL-101 catalyst (Figure 2). The gas released during the reaction was passed through a trap containing 10 M NaOH solution to ensure the complete absorption of CO₂. Carbon monoxide (CO), which is known to poison fuel cell catalysts, was detected by mass spectrometry (MS). The present catalytic activity and selectivity are comparable to those of reported carbon-supported Au–Pd catalysts under similar conditions. It should be noted that subsequent addition of the same amount of formic acid after the completion of the first run resulted in additional equimolar H₂, indicating that the catalyst keeps its activity. Furthermore, the kinetics of hydrogen generation from formic acid improved with increasing temperature, and complete conversion was achieved at all of the temperatures studied (80, 90, and 100 °C).

Factors such as the structure, composition, and morphology of the catalyst and the interaction between the metal NPs and their support influence the catalytic properties of metal catalysts. The preparation using pristine MIL-101 as the support under the same conditions as in the preparation of Au–Pd/ED-MIL-101 afforded the catalyst Au–Pd/MIL-101. The study of its catalytic activity showed that formic acid (140 mg) can be completely converted to H₂ in 145 min (Figure 2), as identified by mass spectrometry. The lower observed catalytic activity of Au–Pd/MIL-101 may be attributed to the decrease in the Pd content in the resultant Au–Pd/MIL-101 catalyst and its larger size of Au–Pd NPs, as confirmed by the inductively coupled plasma (ICP) and transmission electron microscopy (TEM) measurements as mentioned below.

The high-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) point analyses of randomly chosen NPs exhibited the uniform compositions of the Au–Pd alloy NPs in the Au–Pd/MIL-101 and Au–Pd/ED-MIL-101 catalysts. The HAADF-STEM images showed that the sizes of the Au–Pd NPs immobilized by ED-MIL-101 and MIL-101 were in the ranges 2–8 and 2–15 nm, respectively (Figure 3). Small NPs with sizes of 2–3 nm appeared as white dotlike objects inside the mesoporous pores, and the remaining NPs were immobilized on the surfaces of MIL-101 and ED-MIL-101. It should be noted that the probe size for EDX measurements was ~0.5 nm, which is much smaller than the size of the Au–Pd NPs. On the basis of previous reports, the porous structures of these MOFs may offer strict restrictions that confine and prevent the growth of metal NPs on the surface, although the Au–Pd NPs on the surface exhibit a few aggregates with particle sizes larger than that of the MIL-101 pores. In the HAADF-STEM observations, a number of metal NPs existed on the external surface of MIL-101 in Au–Pd/MIL-101, while most of the Au–Pd NPs were found to be smaller than the pore size of the support in Au–Pd/ED-MIL-101, which can be attributed to the introduction of ED into MIL-101. The ED interacts strongly with the metal precursors, which leads to more metal NPs being located in its pores and higher Pd loadings, as confirmed by the ICP results. Both the higher Pd content and smaller particle sizes in Au–Pd/ED-MIL-101 account for the higher rate of hydrogen generation from formic acid.

In order to explore the catalytic properties of different metal NPs immobilized by MIL-101 and ED-MIL-101 in the decomposition of formic acid, we synthesized Ru/MIL-101, Ru–Pd/MIL-101, Pd/ED-MIL-101, Au/ED-MIL-101, Pt/ED-MIL-101, and Au–Pt/ED-MIL-101 under experimental conditions similar to those for Au–Pd/ED-MIL-101 [100 mg of activated support, 100 mg of metal precursor(s), 5 mL of deionized water, 24 h immersion time]. The XPS measurements showed that all the Pd²⁺, Au⁰, Pt⁴⁺, and Ru³⁺ were reduced to metals after H₂ reduction. HAADF-STEM and EDX investigations revealed that the monometallic and bimetallic NPs were immobilized in the MOF supports and that all of the bimetallic NPs were alloys. The study of catalysis showed that Au/ED-MIL-101 and Ru/MIL-101 had no catalytic activity (Figure 2). Pd/ED-MIL-101 and Ru–Pd/MIL-101 released 58 and 14% hydrogen, respectively, from formic acid at 90 °C. Pt/ED-MIL-101 and Au–Pt/ED-MIL-101 released 10 and 14% hydrogen, respectively, from formic acid at 90 °C. MIL-101 and ED-MIL-101 were inactive for
the decomposition of formic acid. From the catalytic properties of Pd/ED-MIL-101, Au/ED-MIL-101, and Au−Pd/ED-MIL-101, it can be considered that the synergetic interaction between Pd and Au plays an important role in the decomposition of formic acid.

Catalyst poisoning induced by CO is an inherent shortcoming for a number of catalytic reactions including CO as a reactant, an impurity in the reactant, or a reaction product, as observed for the fuel cell anode catalysts. We studied the influence of CO poisoning on Au−Pd/ED-MIL-101 and Pd/ED-MIL-101 in the catalytic decomposition of formic acid. Our results show that the Au−Pd/ED-MIL-101 catalyst exposed to CO still showed high activity in the decomposition of formic acid, whereas the Pd/ED-MIL-101 catalyst was completely deactivated by exposure to CO. It can be seen that Au plays a key role in the high tolerance of Au−Pd/ED-MIL-101 with respect to CO poisoning. Since the adsorption strength of CO on Au is much smaller than that of CO on Pd, Au does not form stable complexes with CO. Adsorption strength of CO on Au is much smaller than that of liquid-phase chemical hydrogen storage materials. High-performance catalysts for the generation of hydrogen from formic acid for chemical hydrogen storage. The present results might bring new opportunities in the field of fuel cell anode catalysts.

*Author Contributions*

§The authors thank AIST and JSPS for a postdoctoral fellowship.

**Acknowledgment**

We studied the influence of CO poisoning on Au−Pd/ED-MIL-101 and Pd/ED-MIL-101 in the catalytic decomposition of formic acid. Our results show that the Au−Pd/ED-MIL-101 catalyst exposed to CO still showed high activity in the decomposition of formic acid, whereas the Pd/ED-MIL-101 catalyst was completely deactivated by exposure to CO$^{11}$. It can be seen that Au plays a key role in the high tolerance of Au−Pd/ED-MIL-101 with respect to CO poisoning. Since the adsorption strength of CO on Au is much smaller than that of CO on Pd, Au does not form stable complexes with CO. Adsorption strength of CO on Au is much smaller than that of liquid-phase chemical hydrogen storage materials. High-performance catalysts for the generation of hydrogen from formic acid for chemical hydrogen storage. The present results might bring new opportunities in the field of fuel cell anode catalysts. Further work is needed for developing low-cost, high-performance catalysts for the generation of hydrogen from formic acid because of the CO poisoning. It can be considered that the synergetic interaction between Pd and Au plays an important role in the decomposition of formic acid.

**Supporting Information.** Experimental procedures; PXRD, MS, HAADF-STEM, XPS, ICP, EA, and EDX data; and the results of catalytic formic acid decomposition experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) See the Supporting Information.
