



Short communication

Hydrogen generation at ambient conditions: AgPd bimetal supported on metal–organic framework derived porous carbon as an efficient synergistic catalyst



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ABSTRACT

An efficient synergistic catalyst, AgPd bimetal supported on metal–organic framework derived porous carbon (AgPd/MOF-5-C), was fabricated for the first time. The catalyst exhibited 100% H₂ selectivity and high catalytic activity in hydrogen generation from formic acid at ambient conditions. The initial turnover frequency could reach as high as 854 h⁻¹. The combination of distinct interaction among bimetal, support and high dispersion of nanoparticles drastically enhances the catalytic performance of the resulted catalyst.

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1. Introduction

Now, the traditional energy systems that are mostly based on fossil fuels, which has considerable negative environmental impact, should ideally be replaced with systems based on renewable resource. Among the various alternative energy strategies, hydrogen is a secondary energy carrier and considered to be a globally accepted clean fuel [1]. However, storage and release hydrogen in a safe and efficient way still remain challenging issues. During recent decades, one of the most promising strategies to store hydrogen entails the interconversion of H₂ and CO₂, as illustrated in Scheme 1. This approach offers direct access to regenerative energy carriers based on waste material from the energetic use of fossil fuels [1,2].

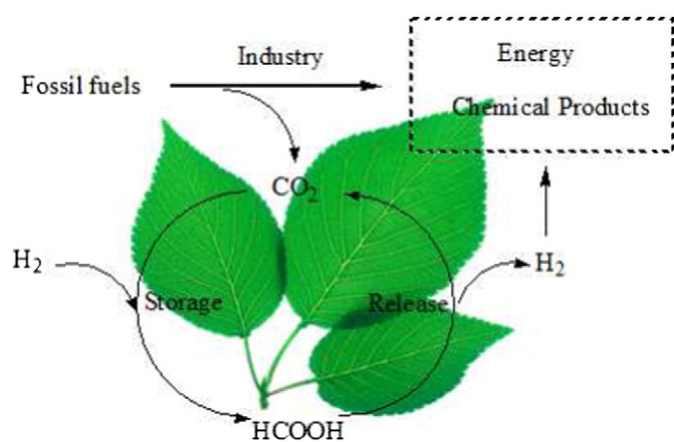
In above approach, the key of applying this strategy was the storage medium, formic acid (FA). FA has limited uses which include its application as an antifungal agent and preservative as well as in the production of leather and as a lime scale remover. It may be produced by chemical methods such as the hydrolysis of methyl formate but it also produced in equimolar proportions, together with levulinic acid, by the hydrolysis of biomass-derived cellulosic raw materials [3]. With the increasing interest in the hydrogenation of CO₂/carbonates to FA/formate [4] and the dehydrogenation of FA in the presence of suitable catalysts [5], FA has been regarded as a kind of promising hydrogen-storage material.

Recently, several homogeneous catalysts have been developed that are able to generate enough CO-free hydrogen at room temperature [6,7]. However, these homogeneous catalytic systems have significant disadvantages: the separation and reusability issues associated with these catalysts hinder their use in practical applications. Heterogeneous catalysts could potentially avoid these drawbacks. Among the heterogeneous catalysts for the dehydrogenation of formic acid, much attention has been paid to monometallic and polymetallic nanoparticles supported on different materials, such as Al₂O₃ [8], ZrO₂ [9], Vulcan XC-72 Carbon [10], reduce graphene oxide [11], macroreticular basic resin [12], ZSM-5 [13], metal–organic framework [14], SiO₂ [15,16] and so on [17], with gold, palladium, platinum and other elements as active ingredients [7,18]. Lately, supported AgPd [11,12,14,17], AuPd [19–21] and PdNiAg polymetallic catalyst [22] have been applied in the decomposition of FA. Despite recent progress, the development of highly selective and active heterogeneous catalysts for the dehydrogenation of formic acid under mild conditions is still desirable for practical use.

It is well known that the synergistic interaction between metal and support, the dispersity of the metal particles, and the type of support play a key role for the catalytic activity of the nanocatalyst. Carbon materials, especially nanoporous carbon materials, have been the most important and traditionally support for heterogeneous catalyst due to their high specific surface area and large pore volume in combination with excellent thermal, chemical and mechanical stability. Recently, metal–organic frameworks (MOFs) have received great interest as a novel class of crystalline nanoporous materials [23]. MOFs with fascinating diverse structures, topologies, permanent nanoscale porosity, high surface

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Scheme 1. An attractive method for storing hydrogen by formic acid.

area and uniform structured cavities, have been demonstrated to be ideal sacrificial templates for fabricating nanoporous carbons [24,25]. The MOFs-derived carbon materials (MOF-C) present high specific surface area, large pore volume, excellent electrochemical performance and high thermal stability, and show excellent properties in gas storage, catalysis, electrode material and adsorbent.

The MOF-5 framework is one of the most representative MOFs in which oxocentered Zn_4 tetrahedra are connected through linear terephthalic acid to give a cubic network structure and three-dimensional channel system [26]. The terephthalic acid in MOF-5 is rich in carbon and therefore it can serve as both carbon precursor and template for the synthesis of nanoporous carbon materials.

In this paper, a nanoporous carbon (MOF-5-C) was prepared by the direct carbonization of MOF-5 as both the precursor and template. Then, AgPd bimetal was supported on MOF-5-C for the first time. The performance of AgPd/MOF-5-C was evaluated by catalyzing the dehydrogenation of formic acid. The results demonstrated that a complete and efficient H_2 generation without CO contamination from FA in FA/SF (SF, sodium formate) solution was achieved at ambient temperature.

2. Experimental

2.1. Synthesis of MOF-5-C

MOF-5 nanocrystal was prepared according to the reported procedure [27] which was illustrated in supporting information. For the synthesis of MOF-5-C, MOF-5 was directly carbonized at various temperatures (700, 800, 900, 1000 °C) under a flow of nitrogen gas. After the carbonization, the obtained black sample was immersed in 10% HCl for 24 h. Then the sample was centrifuged and washed with

distilled water. Finally, the MOF-5-C was obtained by vacuum drying at 80 °C overnight.

2.2. Synthesis of AgPd/MOF-5-C catalysts

The catalyst preparation process was illustrated in Scheme 2. For the preparation of $Ag_3Pd_{12}/MOF-5-C-900$, 50 mg of MOF-5-C-900 was added to 15 mL of $AgNO_3$ (0.0164 mmol) solution containing newly prepared H_2PdCl_4 (0.0665 mmol). The mixture was stirred for 12 h at ambient temperature to impregnate the metal salts. Then, 0.362 g $NaBH_4$ dissolved in 5 mL water was added into the above obtained solution immediately with vigorous stirring. The mixture was stirred for 1.5 h at room temperature. After centrifugation and washing with water, the obtained solid $Ag_3Pd_{12}/MOF-5-C-900$ (the total mass content of metals was 15% and the mass ratio of Ag and Pd was 1:4), was dried at 80 °C in vacuum overnight.

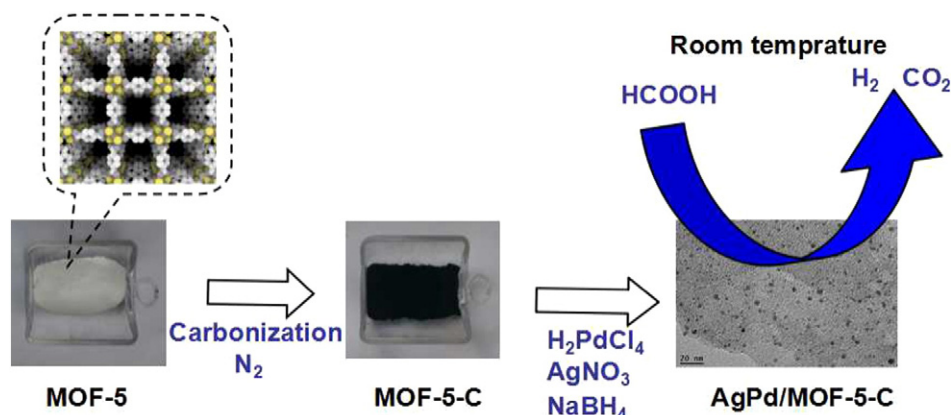
The $Ag_3Pd_{12}/MOF-5-C-700$, $Ag_3Pd_{12}/MOF-5-C-800$, $Ag_3Pd_{12}/MOF-5-C-1000$ (the n represents the carbonization temperature) and $Ag_3Pd_{12}/XC-72$ were fabricated with the same procedure except that 50 mg of MOF-5-C-700, MOF-5-C-800, MOF-5-C-1000 and Vulcan XC-72 Carbon was added, respectively. The $Pd_{15}/MOF-5-C-900$, $Ag_6Pd_9/MOF-5-C-900$ and $Ag_{15}/MOF-5-C-900$ catalysts were synthesized with the above procedure (the total mass content of metals was 15%) except that the theoretical mass ratios of Ag and Pd were 0:5, 2:3 and 5:0, respectively. The synthesis of Ag/Pd/MOF-5-C and AgPd alloy nanoparticles [28] was illustrated in supporting information.

2.3. General procedure for the dehydrogenation of formic acid

Reaction apparatus for measuring the H_2 - CO_2 evolution from FA decomposition is the same as previously reported [14,17]. In general, a mixture of the as-prepared catalyst (8 mg) and distilled water (0.5 mL) was placed in a round-bottomed flask (25 mL), which was placed in a water bath at a preset temperature (25–50 °C) under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The reaction started when 0.5 mL of the mixed aqueous solution containing 1.25 mmol FA and 3.75 mmol SF was injected into the mixture using a syringe. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette. The molar ratios of metals/FA were theoretically fixed at 0.01 for all the catalytic reactions.

3. Results and discussion

The morphology of the as-prepared $Ag_3Pd_{12}/MOF-5-C-900$ composite is characterized by TEM. It can be seen that the AgPd nanoparticles supported on MOF-5-C are well dispersed with an average particle size of about 4 nm (Fig. 1a), suggesting that MOF-5-C leads to the



Scheme 2. Schematic illustration of the catalyst preparation and catalytic dehydrogenation reaction.

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