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An effective low Pd-loading catalyst for hydrogen generation from formic acid

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ABSTRACT

As an interesting hydrogen carrier, formic acid is bio-renewable, non-toxic and available in the liquid state at room temperature. The development of active and low-cost catalyst is of significance for hydrogen generation from formic acid. In this study, both a relatively cheap metal (Ag) and a functional support (nitrogen modified reduced graphene oxide, N-rGO) were applied to prepare Pd catalyst. It was found that the Ag atoms facilitated the formation of Pd-rich surface in the preparation strategy, in which the reductive N-rGO and a two-step feeding process of metal precursors played important roles. In addition, Ag additive was found to benefit catalyst stability. Most interestingly, the obtained low Pd-loading Pd₁Ag₆/N-rGO catalyst showed a specific Pd loading turnover frequency of 171 mol Pd⁻¹ h⁻¹ and a specific metal cost turnover frequency of 64.2 \$⁻¹ h⁻¹, which were predominant among currently available Pd-based catalysts towards formic acid decomposition without any additive under room temperature.

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Introduction

Hydrogen and its combination with the electrochemical energy conversion technology such as fuel cells and electrolyzers, have the potential to provide a reliable, secure and clean energy technology. A significant challenge for use of hydrogen as an energy carrier is an economic production of hydrogen. The industrial production of hydrogen is primarily based on steam reforming from fossil hydrocarbons i.e. natural gas, oil and coal [1]. Water electrolysis, on the other hand, provides a favorable means of hydrogen production in association with use of the surplus electrical energy of renewable sources [2]. Another challenge is a practical approach to store

hydrogen particularly on board for automobile applications. The well-developed hydrogen storage technologies include compressing hydrogen gas in a pressure range of 300–700 bars, liquefying hydrogen down to a temperature below 20.3 K, or storing hydrogen chemically in compounds or physically via metal hydrides [3].

In combination of hydrogen storage and generation formic acid has been identified as an interesting liquid hydrogen carrier. Formic acid, a simple molecule of HCOOH, contains 4.4 wt. % of hydrogen, slightly lower than the DOE 2015 target (5.5 wt. %). Its volumetric capacity of hydrogen is 52 g/l under standard temperature and pressure, higher than most other hydrogen storage materials available today [4]. In addition,

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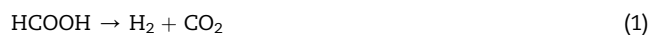
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formic acid as a liquid is easy to handle, relatively low in toxicity. From a safety point of view, formic acid has a flash point 69 °C, compared to –40 °C for gasoline and 13 °C for ethanol, and 85% formic acid is not flammable at all. The most interesting is that formic acid can readily decompose with help of catalysts [4–7]. Chemically, formic acid can be decomposed via dehydrogenation releasing hydrogen and carbon dioxide (Eq. (1)) or via dehydration to form water and carbon monoxide (Eq. (2)):



For direct applications in low temperature fuel cells, CO-free hydrogen is preferred as any traces of CO in the hydrogen fuel would strongly poison the anode catalyst and deteriorate the overall fuel cell performance [8]. It is therefore demanding for catalyst materials that are both highly active and extremely selective toward the dehydrogenation reaction.

The active heterogeneous catalysts are generally based on noble metals e.g. Pd [9–15], Pt [15–17] and Au [9,18,19], among which Pd attracts the most attentions due to its relatively high activity [6,7]. One of the current research targets on Pd catalyst is improving Pd utilization and therefore reducing catalyst cost. The traditional strategy is to decrease nanoparticle size of catalyst [12,13]. However, it is not feasible to limitlessly decrease particle size because ultrafine-size particles are

easily aggregated due to the high surface energy [20]. Moreover, both linear and multi-linear adsorption modes of formic acid on catalyst, which would lead to stronger chemisorption and CO formation, tend to exist on small nanoparticles [6]. Another efficient strategy is to construct Pd-based alloys [6,21–32]. Surface electronic properties of Pd could be modified due to the lattice expansion/shrinkage while the other metal atoms might play a role of dispersion agent for the Pd atoms. For example, the catalytic performance of Pd was dramatically improved by coating a thin layer of Pd atoms onto the surface of Ag nanoparticles [6]. The introduction of Co into PdAg [23] or PdAu [24] catalysts exhibited an electronic effect on Pd atoms and thought to be beneficial for the catalytic activity towards formic acid decomposition. Introducing of support other than active carbon into the Pd-based catalyst was also an available strategy to increase the catalyst utilization. For example, graphene is an idea alternative support due to its high surface area, fast charged carrier mobility and high stability. At the same time, the positive effect of graphene could be enlarged by substitutional doping heteroatoms such as nitrogen atoms into the carbon lattice of graphene [30,32]. This nitrogen doping is able to increase the support–catalyst interaction for improved catalyst durability, benefit the construction of composite material, modulate the electronic structure of both carbon and catalyst particle to enhance the intrinsic catalytic activity [33,34]. Especially, graphene was found to have reducing property and has potential as reducing agent for synthesis of metal nanoparticles such as Pd, Pt and PdAg [30,35–37].

In this study, both nitrogen modified reduced graphene oxide (N-rGO) and second metal (Ag) were employed to

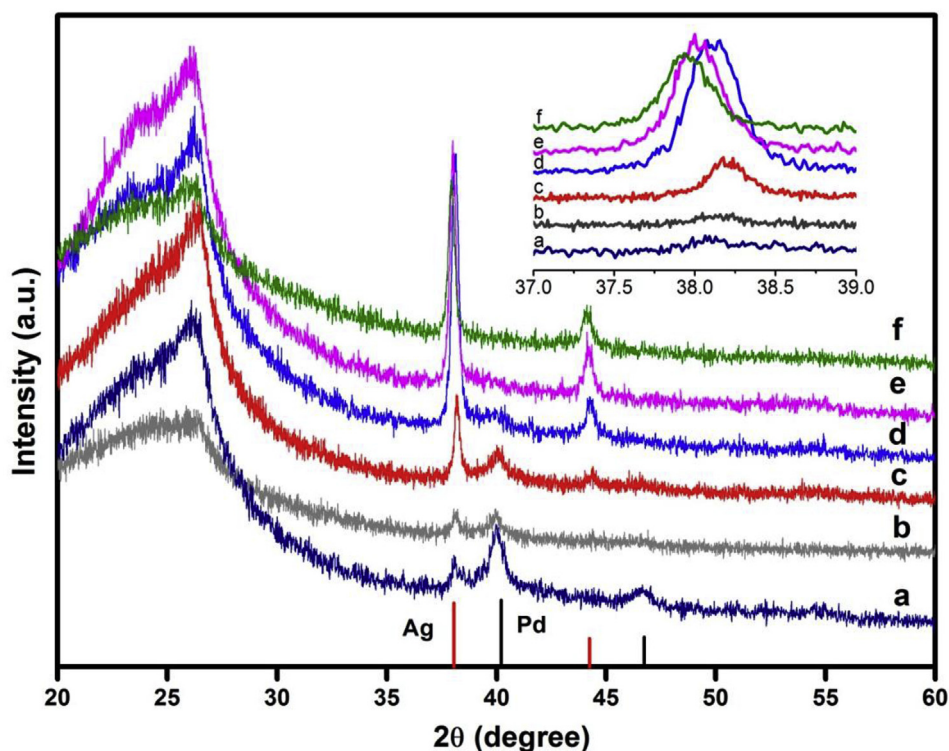


Fig. 1 – XRD patterns of PdAg/N-rGO catalysts prepared with different Pd/Ag molar ratios in the precursors: (a) Pd₂Ag₁/N-rGO, (b) Pd₁Ag₁/N-rGO, (c) Pd₁Ag₂/N-rGO, (d) Pd₁Ag₄/N-rGO, (e) Pd₁Ag₆/N-rGO and (f) Pd₁Ag₈/N-rGO.

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