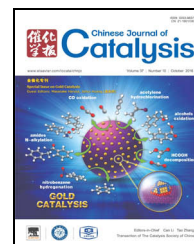


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Minireview (Special Issue on Gold Catalysis)

Gold-containing metal nanoparticles for catalytic hydrogen generation from liquid chemical hydrides

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ABSTRACT

Liquid chemical hydrides, which store hydrogen in the form of chemical bonds, are considered one of the most promising classes of hydrogen storage materials. Their application depends heavily on the development of efficient catalytic systems. Gold-containing metal nanoparticles have exhibited excellent catalytic performance for hydrogen generation from liquid chemical hydrides. The present mini-review focuses on recent developments in hydrogen generation from liquid chemical hydrides using gold-nanoparticle and gold-containing heterometallic nanoparticle catalysts.

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1. Introduction

Hydrogen is considered a clean, effective and renewable energy carrier for a sustainable future [1–3]. In particular, hydrogen fuel cells can efficiently generate electricity to power vehicles and other devices without any emission of regulated gas pollutants [4–6]. Over the past decades, several advanced storage systems, such as cryogenic liquid cylinders, high-pressure gas cylinders and porous materials including zeolites, carbons and metal-organic frameworks have been developed for hydrogen storage [7–10]. However, these systems still face practical challenges in that they are not able to meet the demands required for practical applications because of their technological limits in safety (high pressure, low temperature) and density (low volumetric/gravimetric hydrogen densities).

Recently, concepts for hydrogen production from liquid

chemical hydrides, such as formic acid and ammonia borane, have gained considerable interest [11–13]. Since hydrogen is stored in a safe and stable manner in the form of chemical bonds, liquid chemical hydrides possessing high hydrogen contents are easy to handle. Additionally, as liquid chemical hydrides have similar characteristics to common fuels, they can be effectively employed into already existing infrastructures. A number of homogeneous and heterogeneous catalysts with very high catalytic activities have been investigated for hydrogen generation from liquid chemical hydrides [14–18].

Since the report on the catalytic oxidation of CO using gold nanoclusters by Haruta in the 1980s, gold catalysts have attracted a wealth of interdependent research [19–22]. Hitherto, significant progress of gold catalysis has been achieved for various reactions [23–26]. Not only monometallic gold catalysts but also gold-containing heterometallic nanoparticles (NPs) have shown superior catalytic performance for various

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reactions, involving catalytic hydrogen generation from liquid chemical hydrides. In this mini-review, we detail the recent advances in the utilization of gold NPs and gold-containing metal alloy and core-shell NPs as catalysts for hydrogen generation from liquid chemical hydrides, formic acid (HCOOH) and ammonia borane (NH_3BH_3).

2. Formic acid dehydrogenation

Formic acid, as a promising hydrogen carrier, has several remarkable features to include: (1) nontoxicity with a high hydrogen content (4.4 wt%), (2) high stability as a liquid at room temperature, and (3) the availability *via* various synthesis routes, e.g., biomass process, CO_2 hydrogenation or methyl formate hydrolysis [27–30]. Typically, suitable catalysts are used to facilitate formic acid decomposition *via* dehydrogenation ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$, $\Delta G_{298\text{K}} = -48.8 \text{ kJ}\cdot\text{mol}^{-1}$) for practical applications, rather than dehydration ($\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$, $\Delta G_{298\text{K}} = -28.5 \text{ kJ}\cdot\text{mol}^{-1}$), which produces the CO impurity that is toxic to fuel cell catalysts [31,32].

Monometallic gold NPs, as efficient heterogeneous catalysts for formic acid dehydrogenation, have received tremendous attention, owing to their high activity, ease of separation and efficient recycling [33]. We have reported amine-functionalized silica nanospheres encapsulated gold NPs as catalysts for hydrogen generation from formic acid [34]. Unlike gold NPs encapsulated in silica nanospheres in the absence of functional amine groups, the gold NPs encapsulated in the amine-functionalized counterparts show very high activity for the dehydrogenation of formic acid, releasing CO-free hydrogen with fast kinetics at 90 °C (Fig. 1). The strong metal-molecular support interaction (SMMSI) between the encapsulated gold NPs and the amine-functionalized SiO_2 spheres was suggested as the reason for the high catalytic activity. It has been demonstrated that the acid-tolerant ZrO_2 -supported gold nanocluster (~1.8 nm) catalysts can facilitate the liberation of CO-free hydrogen from formic acid-amine mixtures with a high turnover frequency (TOF) of 1590 h^{-1} at 50 °C under ambient conditions [35]. Most recently, Zhang and co-workers [36] developed

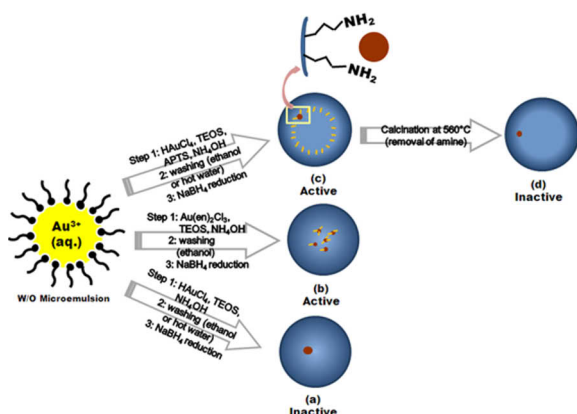


Fig. 1. Microemulsion-based syntheses of gold nanocatalysts encapsulated within hollow silica nanospheres of Au@ SiO_2 (a), Au@ SiO_2 _EN (b), Au@ SiO_2 _AP (c), and Au@ SiO_2 _AP_C (d). Reproduced from Ref. [34] with permission. Copyright Royal Society of Chemistry, 2012.

Schiff base-functionalized gold NPs for the catalytic dehydrogenation of high-concentration formic acid in the absence of additives. The reactions proceeded efficiently with a high TOF of 4368 h^{-1} in 10 mol L^{-1} formic acid solutions at 50 °C. The enhanced catalytic feature was assigned to the C-H activation between the protonated Schiff base and electronegative gold NPs at the interface.

Gold-containing metal alloy NPs have also been reported to be superior catalysts for dehydrogenation of formic acid. Xing and co-workers [37] used carbon supported AuPd NPs with an average particle size of ~3.5 nm for the decomposition of formic acid, and achieved high activity, although a minor trace of CO was generated. The catalytic performance was further improved by introducing CeO_2 as a promoter, and a maximum TOF of 832 h^{-1} was obtained at 102 °C. Furthermore, Mullins and co-workers [38] confirmed that the bimetallic AuPd alloy NPs were excellent catalysts for formic acid dehydrogenation because of appropriate synergetic effects. Most recently, by using a Mg^{2+} -assisted low temperature reduction approach, Chen and co-workers [39] have successfully immobilized small AuPd alloy NPs on carbon supports for hydrogen generation from formic acid, which achieved an initial TOF of 1120 h^{-1} at room temperature without CO emission.

Recently, various advanced functional materials have been explored as supports to further improve the catalytic performance of gold-containing metal alloy NPs. Porous metal-organic frameworks (MOFs) have proved to be unique hosts to encapsulate metal NPs with controlled particle sizes and distributions [40–42]. We have employed MIL-101, one of the representative MOFs, and its ethylenediamine-grafted counterpart to support AuPd alloy NPs, which were used as highly active catalysts for the complete conversion of formic acid. The synergistic effects between Au and Pd were observed in this bimetallic AuPd NP and a high tolerance with respect to CO poisoning was obtained [43]. This work also drew increased interest in MOF-immobilized NPs as catalysts for formic acid decomposition [44–46]. Graphene, a single-layer sp^2 -hybridized carbon sheet, has recently been considered as a promising metal NP catalyst support because of its large surface area and excellent stability [47–50]. Yan and co-workers [51] have shown that the N-doped reduced graphene oxide (rGO) can be used as an excellent support for immobilizing ultrafine AuPd-CeO₂ nanocrystals for formic acid dehydrogenation. They further prepared a bi-support consisting of ZIF-8 and rGO to immobilize AuPd-MnO_x NPs, which showed high catalytic activity in formic acid dehydrogenation with an initial TOF of 382.1 h^{-1} at 25 °C in the absence of additives [52]. Very recently, we reported a highly active rGO-supported AuPd alloy nanoparticle catalyst synthesized using a non-noble metal sacrificial approach (NNMSA) for hydrogen production from formic acid [53]. As highly dispersed AuPd NPs were successfully immobilized on the rGO by the sacrifice of the co-precipitated $\text{Co}_3(\text{BO}_3)_2$, our catalysts exhibited the highest TOF of 4840 h^{-1} at 50 °C with no trace of CO emissions (Fig. 2).

Recently, considering the reduction of consumption of the noble metals, a trimetallic system consisting of Co, Au and Pd has been studied for the dehydrogenation of formic acid at

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