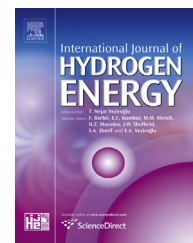




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Promoted hydrogen generation from formic acid with amines using Au/ZrO₂ catalyst

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ABSTRACT

Decomposition of formic acid (FA) to hydrogen and carbon dioxide through catalysis holds great promise for clean energy in fuel cells designed for portable use, but the selective and efficient dehydrogenation of FA by a robust heterogeneous catalyst under ambient conditions remains a major challenge. We report herein that a new FA dehydrogenation system comprising liquid FA and amines with high boiling point as hydrogen storage material can be efficiently decomposed for ultrapure H₂ release under mild reaction conditions. Of significant importance is that a high turnover frequency (TOF) of up to 1166 h⁻¹ can be readily attained at 60 °C in FA-dimethylethanolamine system using gold nanoparticles supported on amphoteric zirconia (Au/ZrO₂). The amine acts as a proton scavenger can facilitate the O–H bond cleavage in the key step of FA deprotonation in Au–ZrO₂ interface resulting in high catalytic activity. The versatile gold catalyst displayed excellent stability for dimethylethanolamine-assisted FA dehydrogenation as well as a typical particle-size-dependent effect.

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Introduction

Hydrogen, a green energy vector, has been considered as an ideal potential candidate to solve both the global energy and environmental problems [1–4]. However, because of its low boiling point and low volumetric energy density at atmospheric conditions, H₂ is difficult to store in compressed or liquid form and hard to transport with safe manner, and

these are both of the major challenges in establishing a hydrogen economy [5,6]. Although many porous materials can be used for physical hydrogen storage, hydrogen capacities of the materials limit their further applications [7–10]. In chemical hydrogen storage, formic acid (HCOOH, FA) has been identified as one of the most important liquid compounds for safe and convenient hydrogen storage in fuel cells designed for portable use owing to its considerable

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hydrogen content (53 g L^{-1}), nontoxicity and high stability under ordinary conditions [11–15]. It is known that the chemical decomposition of FA proceeds via two main pathways, i.e., the dehydrogenation process to form H_2 and CO_2 , and the dehydration one to form H_2O and CO (Scheme 1) [16–20]. Under the design and preparation of catalyst used, the activity and selectivity of hydrogen generation can be strongly controlled and the production of CO impurity can also be strictly constrained.

Much progress has been made both on the homogeneous and heterogeneous catalysis for the selective dehydrogenation of FA [21–49]. And the heterogeneous catalysts have attracted increasing interest owing to the advantage of operating at ambient atmosphere as well as facile separation and recycling [28–49]. In an overview of literature, Au and Pd are more active than other analogous solids [28–49]. Xu et al. grafted the electron-rich functional group ethylenediamine (ED) into metal-organic frameworks (MOFs) MIL-101 to immobilize bimetallic Au–Pd nanoparticles (NPs) showing the turnover frequency (TOF) of 106 h^{-1} at $90 \text{ }^\circ\text{C}$ [31]. A trimetallic PdAuEu/C was demonstrated by Xing and co-workers displayed the activity of 387 h^{-1} at $92 \text{ }^\circ\text{C}$ for FA dehydrogenation [28]. However, the high performance observed from these catalysts could only be achieved at high temperatures ($>80 \text{ }^\circ\text{C}$) for liquid FA decomposition and the kinetic properties of FA dehydrogenation under ambient conditions still need to be further promoted. Apart from the optimization of catalysts, great efforts have also been made on the development of FA decomposing reaction system [28,31–34,50]. For example, extra additives, such as various organic amines and sodium formate or potassium formate were conventionally used as proton scavenger to facilitate the O–H bond cleavage and thus leading to the formation of a metal-formate species during the initial step of the overall dehydrogenation process [28,31–34,50].

More recently, we have found that a simple Au-based catalyst (Au/ZrO_2) can efficiently release the H_2 stored in liquid FA under ambient conditions [50]. With this versatile gold material, controlled and efficient CO -free H_2 liberation from a FA-amine (FA/NET_3 with molar ratio of 5/2) mixture can be readily achieved. However, the promoter of NET_3 with low boiling point ($89.5 \text{ }^\circ\text{C}$) can be volatilized in the FA decomposition process and the generated H_2 gas with volatile organic compounds (VOCs) could not be directly adapted to downstream practical applications such as fuel-cell-based technologies for clean power generation [50]. Therefore, it is necessary to search a base promoter with high boiling point to assist FA dehydrogenation showing no or extremely trace volatile gas. Herein, we present a profile

for screening assisted amines with high boiling point for promoting hydrogen generation from FA and describe the influence of organic bases on the activity of the Au-catalyzed dehydrogenation of FA. Besides the nature of the amine, its ratio to FA also controls the performance of the catalyst system.

Experimental

Catalyst preparation

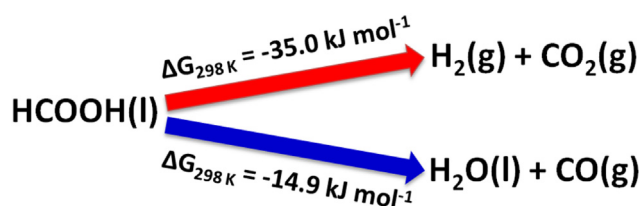
ZrO_2 (56% monoclinic and 44% tetragonal phase) powders were prepared with a conventional precipitation method following the previous procedure [50]. 8.0 g zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Alfa Aesar, 99%) was dissolved in 200 mL deionized water and the pH was adjusted to approximately 9.5 by dropwise addition of 2.5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Aldrich, 28%) under stirring at room temperature. The resultant hydrogel was thoroughly washed with deionized water until free of Cl^- after stirring for 8 h. The precipitate was then dried at $100 \text{ }^\circ\text{C}$ for 12 h followed by calcination at $400 \text{ }^\circ\text{C}$ (ramping rate of $10 \text{ }^\circ\text{C min}^{-1}$) in air for 2 h to obtain the final material.

A modified deposition-precipitation (DP) procedure has been used to prepare the Au/ZrO_2 samples [50]. Briefly, 2.0 g ZrO_2 powders were dissolved with 100 mL 1 mM (or 1.6 mM) of aqueous solution of HAuCl_4 (Alfa Aesar, 48 wt% Au), and the pH was adjusted to 9.0 by dropwise addition of 0.25 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ (CAUTION: the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ to HAuCl_4 solution may give rise to highly explosive fulminating gold). After 6 h (or 12 h or 24 h) stirring at room temperature, the catalyst was washed six times with deionized water until free of Cl^- (using AgNO_3 solution for test) and separated by filtration. The samples were dried at $110 \text{ }^\circ\text{C}$ in air for 1 h, followed by a careful treatment with a stream of 5 vol% H_2/Ar at $300 \text{ }^\circ\text{C}$ (ramping rate of $5 \text{ }^\circ\text{C min}^{-1}$) for 2 h. The Au loading was determined to be 0.8 wt% by ICP-AES.

The Au/ZrO_2 catalyst with subnanometric gold particle size of about 0.8 nm was prepared following the abovementioned method under milder conditions [50]. Basically, 1.0 g ZrO_2 powder was dispersed into 200 mL 0.25 mM of aqueous solution of HAuCl_4 , the pH of which was adjusted to 9.0 by dropwise addition of 0.25 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. After 6 h stirring at room temperature, the catalyst was washed six times with deionized water until free of Cl^- (using AgNO_3 solution for test) and separated by filtration. The sample was then dried at $25 \text{ }^\circ\text{C}$ under vacuum for 12 h, followed by a careful treatment with a stream of 5 vol% H_2/Ar at $250 \text{ }^\circ\text{C}$ (ramping rate of $5 \text{ }^\circ\text{C min}^{-1}$) for 2 h.

Catalyst characterization

The BET specific surface areas of the catalysts were determined by adsorption–desorption of nitrogen at $-196 \text{ }^\circ\text{C}$, using a Micromeritics TriStar 3000 equipment. Sample degassing was performed at $300 \text{ }^\circ\text{C}$ prior to acquiring the adsorption isotherm. Actual Au loading of the catalysts was measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Thermo Electron



Scheme 1 – Two pathways of formic acid decomposition.

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