



Gold supported on zirconia polymorphs for hydrogen generation from formic acid in base-free aqueous medium



Qing-Yuan Bi^{a, b}, Jian-Dong Lin^a, Yong-Mei Liu^a, He-Yong He^a, Fu-Qiang Huang^{b, c},
Yong Cao^{a, *}

^a Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai, 200433, PR China

^b State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, PR China

^c Beijing National Laboratory for Molecular Sciences and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, PR China

H I G H L I G H T S

- ZrO₂ polymorphs possess markedly different amount of surface acidity and basicity.
- The basic sites of gold catalyst are crucial for the cleavage of O–H bond of HCOOH.
- Au/m-ZrO₂ shows excellent reaction rate of 81.8 L H₂ g_{Au}⁻¹ h⁻¹.
- The H/D exchange between HCOOH and H₂O in reaction system is observed.

A R T I C L E I N F O

Article history:

Received 18 May 2016

Received in revised form

28 July 2016

Accepted 10 August 2016

Available online 17 August 2016

Keywords:

Gold catalysis

Zirconia polymorphs

Formic acid

Base-free

Hydrogen

A B S T R A C T

Formic acid (FA) has attracted considerable attention as a safe and convenient hydrogen storage material for renewable energy transformation. However, development of an efficient heterogeneous catalyst for selective FA decomposition for ultraclean H₂ gas in the absence of any alkalis or additives under mild conditions remains a major challenge. Based on our previous work on Au/ZrO₂ as a robust and efficient catalyst for FA dehydrogenation in amine system, we report here ZrO₂ with different nanocrystal polymorphs supported Au nanoparticles can achieve near completion of FA dehydrogenation in base-free aqueous medium. Of significant importance is that an excellent rate of up to 81.8 L H₂ g_{Au}⁻¹ h⁻¹ in open system and highly pressurized gas of 5.9 MPa in closed one can be readily attained at 80 °C for Au/m-ZrO₂. *In situ* diffuse reflectance infrared Fourier transform (DRIFT) and CO₂-temperature programmed desorption (TPD) techniques revealed that Au/m-ZrO₂ exhibits a higher density of surface basic sites than Au/t-ZrO₂ and Au/a-ZrO₂. Basic sites in surface can substantially facilitate crucial FA deprotonation process which appears to be a key factor for achieving high dehydrogenation activity. The H/D exchange between solvent of H₂O and substrate of FA was observed by the kinetic isotope effect experiments.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen is considered as a promising alternative to satisfy the increasing demands for an efficient and clean energy supply [1–4]. However, the practical realizations of controlled storage and release of hydrogen are still of great challenges in the fuel cell based

hydrogen economy [5,6]. To date, chemical methods for hydrogen storage and use have focused on the use of metal hydrides [7], liquid organic heterocycles (LOH) [8], ammonia borane (AB) [9], alcohols [10], hydrazine [11] et al. as storage materials. Of special interest is the use of bio-renewable formic acid (FA) as hydrogen carrier, not only due to its role in sustainable energy production and renewable chemical synthesis but also for its simplicity which makes it ideal for fundamental bond making and breaking studies [12–15]. It was identified that the decomposition of FA may occur via two distinct reaction pathways, namely the decarboxylation,

* Corresponding author.

E-mail address: yongcao@fudan.edu.cn (Y. Cao).

yielding H_2 and CO_2 ($\text{HCOOH}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$, $\Delta G_{298\text{K}} = -35.0 \text{ kJ mol}^{-1}$) or the dehydration into H_2O and CO ($\text{HCOOH}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}(\text{g})$, $\Delta G_{298\text{K}} = -14.9 \text{ kJ mol}^{-1}$) [16]. Particularly given that the gravimetric energy density of FA is by a factor of 7 superior compared to commercially available lithium ion batteries, FA thus represents a convenient liquid hydrogen carrier in fuel cells designed for portable use [17]. This has prompted great efforts directed toward the catalytic FA decomposition in the liquid phase, where the production of CO-free H_2 at convenient temperatures is of great importance.

Indeed, much progress has been made in the catalytic dehydrogenation of FA by using homogeneous systems, such as Ru [18,19], Ir [20,21], Rh [22], and Fe complexes [23,24]. However, apart from the practical inconvenience arising from the use of sophisticated and expensive ligands, the widespread application of these systems has been severely limited by the intrinsic air-instability and short recyclability. Therefore, tremendous efforts have been devoted to synthesizing high performance solid catalysts. Among different heterogeneous catalyst systems, mono-, bi- and tri-metal active components have been demonstrated as a series of very effective catalysts for hydrogen evolution via FA decomposition due to simple operation, significant durability, and cost-saving [25–35]. Despite their high performance for dehydrogenation, most reaction processes suffering from indispensable additives of various inorganic alkali (sodium or potassium salts), which can lower the gravimetric energy density of FA [27–30,36–39]. From the standpoint of practical application, the use of additive-free aqueous FA as the liquid chemical hydrogen storage material would be beneficial for maximizing the overall deliverable capacity [25,26,31–35]. Moreover, the ultraclean H_2 gas generated from the FA system would also be advantageous to its direct downstream application of fuel-cell-based technologies for clean power generation [40]. Thus, the development of simple, efficient, and recyclable heterogeneous catalyst system for affording facile and selective evolution of ultrapure H_2 gas ($\text{CO} < 10 \text{ ppm}$) from FA in base-free aqueous medium under ambient conditions is highly desired.

Gold-containing catalysts have been extensively employed in past decades for low temperature CO oxidation [41], water-gas shift reactions (WGS) [42], selective oxidation/reduction [43], and fine chemical synthesis [44]. It is also established that gold catalysts are very selective for vapor-phase FA dehydrogenation and gold-based alloy or core-shell structured materials are highly effective for liquid-phase FA decomposition for pure H_2 gas [12,14,26,27,33,35]. During the search for a readily available, applicable, highly active and reusable catalyst for FA dehydrogenation, we have recently found that a simple Au-based catalyst comprising ultrasmall Au nanoclusters dispersed on a biphasic ZrO_2 can efficiently release CO-free H_2 from a FA-amine mixture with controlled manner under ambient conditions, even at room temperature of 25°C [45]. Although the important role played by ZrO_2 in dehydrogenation was noticed when comparing the activity of Au/ ZrO_2 with gold supported on other metal oxides, the fundamental understanding of the essential role of the underlying support, in particular the amphoteric nature of ZrO_2 with different pure crystallite phases, on the origin of the high catalytic activity of Au/ ZrO_2 system is still lacking.

Herein, we report Au nanoparticles (NPs) supported on ZrO_2 with different crystal phases and their catalytic properties for additive-free FA dehydrogenation in the aqueous medium under near ambient conditions. Given the well established fact that polymorphic nature of ZrO_2 strongly influences the performance of a ZrO_2 -based catalyst, the present work aims to identify the crystalline-phase-dependent behavior of the Au/ ZrO_2 systems. To gain an insight into the respective nature of Au and ZrO_2 phases as

well as the structural properties of the Au/ ZrO_2 catalyst in relation to their performance in base-free FA decomposition, extensive characterization by N_2 adsorption, X-ray diffraction (XRD), temperature programmed desorption (TPD), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been carried out.

2. Experimental

2.1. Catalyst preparation

Monoclinic (*m*-) and tetragonal (*t*-) ZrO_2 samples were synthesized at 160°C for 20 h in a Teflonlined stainless-steel autoclave (250 mL) containing solutions (80 mL) of $\text{CO}(\text{NH}_2)_2$ (Aldrich, 99.5%) and $\text{ZrO}(\text{NO}_3)_2$ (Alfa Aesar, 99%) [46]. Deionized water and CH_3OH (Aldrich, 99.9%) were used as solvents for synthesizing *m*- ZrO_2 and *t*- ZrO_2 , respectively. The concentration of Zr^{4+} in the solution was 0.4 M, and the $\text{CO}(\text{NH}_2)_2/\text{Zr}^{4+}$ molar ratio was controlled to be 10. The resulting precipitates were respectively washed thoroughly with water and CH_3OH , and dried at 100°C overnight and calcined at 400°C for 4 h in air. The amorphous (*a*-) ZrO_2 was prepared by a conventional precipitation method following the reported procedure [45]. Briefly, appropriate amount of $\text{ZrO}(\text{NO}_3)_2$ was dissolved in 200 mL deionized water, the pH was adjusted to about 9.5 by dropwise addition of 2.5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Aldrich, 28%) under stirring at 25°C . The resultant hydrogel was washed with deionized water after stirring for 8 h. The precipitate was then dried at 100°C overnight followed by calcination at 300°C in air for 2 h to obtain the final material. The biphasic ZrO_2 (*b*- ZrO_2 , 56% monoclinic phase and 44% tetragonal phase) was prepared following the above-mentioned procedure of *a*- ZrO_2 but using oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) as the zirconium precursor and 400°C as the final calcination temperature.

A modified deposition-precipitation (DP) procedure has been used to prepare the Au/ ZrO_2 samples [45]. Briefly, 2.0 g ZrO_2 powders were dispersed into 100 mL 1 mM of aqueous solution of HAuCl_4 (Alfa Aesar, 48 wt% Au), 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 probably give rise to highly explosive fulminating gold). After stirring for 6 h at 25°C , the catalyst was washed several times with deionized water until free of chloride ions (using AgNO_3 solution for test) and separated by filtration. The samples were dried at 100°C in air for 1 h, and followed by a careful reduction treatment with a stream of 5 vol% H_2/Ar at 300°C for 2 h.

2.2. Catalyst characterization

Actual Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The BET specific surface areas of the prepared catalysts were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300°C prior to acquiring the adsorption isotherm. The XRD information of the catalysts was carried out on a German Bruker D8 Advance X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation at 40 kV and 20 mA, and the crystallite size was calculated according to the Scherrer Equation $D = 0.89\lambda/\text{Bcos}\theta$ ($\lambda = 0.154056 \text{ nm}$). XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode ($\text{Mg K}\alpha$, $h\nu = 1253.6 \text{ eV}$) was used. The C 1s line (284.6 eV) was used as the reference to calculate the binding

Download English Version:

<https://daneshyari.com/en/article/7727281>

Download Persian Version:

<https://daneshyari.com/article/7727281>

[Daneshyari.com](https://daneshyari.com)