



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhe

All-solid-state magnesium oxide supported Group VIII and IB metal catalysts for selective catalytic reforming of aqueous aldehydes into hydrogen

Renhong Li ^{a,*}, Xiaohui Zhu ^a, Leilei Du ^a, Kaicheng Qian ^a, Biling Wu ^a, Satoshi Kawabata ^b, Hisayoshi Kobayashi ^{b,**}, Xiaoqing Yan ^{c,***}, Wenxing Chen ^a

^a Key Lab of Advanced Textile Materials and Manufacturing Technology, Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, China

^b Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, 606-8585, Japan

^c Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, China

ARTICLE INFO

Article history:

Received 7 December 2016

Received in revised form

6 February 2017

Accepted 7 February 2017

Available online xxx

Keywords:

Hydrogen production

Magnesium oxide

Aldehyde

Catalytic reforming

External energy-free

ABSTRACT

Molecular hydrogen is of critical importance in the chemical industry and might play vital role in future for benign and secure energy technologies. However, its generation from renewable sources, such as water and biomass without the addition of external energy (heat, light and electricity) remains difficult. Herein, we report that Group VIII and Group IB transition metal nanoparticles supported on magnesium oxide are active all-solid-state catalyst systems for external energy-free liberation of molecular hydrogen by aldehyde reforming in liquid water at ambient conditions. Based on experimental observation and DFT calculation, it is suggested that molecular oxygen as well as water can be readily reduced on Group IB metals via two-electron process to form peroxy radicals, while most of Group VIII metals such as Pt end up with sites creating oxo species but instead form hydroxyl radicals via four-electron processes. Therefore, by altering supporting metals, we are able to control the reaction pathways (reduction of aldehydes into H₂ or oxidation of aldehydes into CO₂) due to the difference of oxygen reduction products.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Molecular hydrogen (H₂) is of critical importance in the chemical industry and might play vital role in future for benign and secure energy technologies [1–7]. Currently,

more than 95% of H₂ is derived from nonrenewable natural gas, coal and petroleum by means of steam-reforming and coal gasification [8–10], which is neither a long-term solution to current energy problems nor an environment-friendly process. In principle, H₂ could also be generated from renewable resources such as water, while efficient H₂

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: lirenhong@zstu.edu.cn (R. Li), hisa@kit.ac.jp (H. Kobayashi), yanxiaoqing927@zstu.edu.cn (X. Yan).

<http://dx.doi.org/10.1016/j.ijhydene.2017.02.041>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

production from overall water splitting remains highly difficult by conventional electrolysis, thermolysis, photocatalysis, and combinations thereof [11]. All of these methods require external energy input that largely reduces the benefit of these chemical processes for energy supply. In addition, because of the complexity in building complete artificial water splitting system, when investigating the reductive half reaction it is common to use a sacrificial electron/hydrogen donor to optimize H₂ production efficiency [12–15]. In this case, the introduction of biomass into water has been proved to be a powerful technique to achieve efficient H₂ generation (namely, biomass reforming) bypassing the overall water splitting [16–18]. Previous studies have shown that transitional metal-based catalysts can be employed for H₂ production from biomass reforming, while high temperature (>200 °C) is usually acquired to initiate the reaction [19–23], thus consuming a large amount of thermal energy. In order to reduce energy dissipation, the exploration of external energy-free H₂ production (i.e., without the addition of light, electrical or thermal energy) from catalytic reforming of biomass or its derivatives in liquid water is much desirable. In this context, aldehyde is perceived as a suitable sacrificial reagent to realize water reduction [20,24–28]. During the past decade, a number of heterogeneous and homogeneous catalytic systems have been developed for H₂ production from alkaline aldehyde solutions at ambient conditions [29–37]. However, the development of efficient all-solid-state catalysts for external energy-free aldehyde reforming without any base additives remains the main hurdle for practical applications of this approach. Meanwhile, the fundamental chemical principles responsible for the supported metal nanoparticles mediated H₂ generation from various aldehyde aqueous solutions remain controversial.

Herein, we demonstrate that H₂ can be controllably produced from almost all kinds of aldehydes in water at low temperatures (0–25 °C) in an aqueous-phase reforming process using magnesium oxide (MgO) supported transition metal nanocatalysts. MgO is selected as the support because we have demonstrated that it is a superior all-solid-state support for silver nanocatalyst for low temperature formaldehyde reforming into H₂ [38]. Especially, it is found that MgO supported Group IB metal catalysts are excellent for H₂ production. In contrast, supported Group VIII metals, except Pt, are able to dehydrogenate aldehyde solution into H₂ but produce a large amount of CO₂ at the same time. Based on the experimental observation and DFT calculation, it is tempting to conclude that Group IB metal loading creates highly active sites for oxygen and water co-reduction to afford a peroxy species on support surface, which is critical to the dehydrogenation reaction. However, most of Group VIII metals such as Pt loading create oxo species that are inactive for dehydrogenation but active for total oxidation of aldehydes into CO₂. Thus we show that the selectivity for surface redox reaction of aldehydes can be readily tailored by choosing different transition metals. These findings also suggest that catalytic aqueous-phase reforming might prove useful for the generation of hydrogen-rich fuel gas from carbohydrates extracted from renewable biomass and biomass waste streams.

Experimental

Synthesis of MgO

In a typical synthesis of MgO NPs, 6.2 mL of magnesium methoxide and 100 mL of methanol were placed in a sonic bath for 10 min. The mixture was then hydrolyzed with 200 mL of deionized water at 80 °C for 6 h. The resulting hydrolysate was washed by ethanol and deionized water for several times, and collected after centrifuging. The powder was dried at 80 °C overnight and then calcined at 450 °C in air for 5 h.

Synthesis of metal NPs

In a typical synthesis of AgNPs, 110 mg AgCF₃COO was mixed with 250 μL of dodecanethiol in 50 mL of benzene to form a clear solution under a flow of H₂/Ar (5 v/v%) gas, to which 435 mg of borane-tert-butylamine complex (BTBC) was added in one portion. The mixture was heated with stirring at 55 °C for 2 h before the reaction system was cooled to room temperature. AgNPs were precipitated out from the reaction mixture as black solid powders by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol, and dried in H₂/Ar flow. Other metal NPs synthesis methods are listed in the [Supporting information](#).

Synthesis of M/MgO

Desired amount of as-synthesized MNPs were dissolved in 25 mL chloroform, to which a desired amount of MgO was added. After 30 min stirring, the solid product was centrifuged and dried in air. For MgO supported AgNPs, CuNPs, PdNPs and NiNPs, the samples were calcined at 500 °C under a H₂/Ar (5 v/v%) flow for 5 h. For the other samples, direct calcination at 500 °C in air for 5 h was carried out.

Material characterization

High-resolution X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. Nitrogen adsorption–desorption analysis was carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, calcined samples were out gassed under a vacuum at 200 °C in the port of the adsorption analyzer. Transmission electron microscopy (TEM) images were taken using a JEOL 2010 electron microscope operating at 80 keV. Inductively coupled plasma mass spectrometry (ICP-MS) was carried out in Agilent 7700 using the dissolving solution containing calculated M/MgO in nitric acid or aqua regia. X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10 ms. The spin trapping experiments were performed as follows: 5,5–dimethyl-

Download English Version:

<https://daneshyari.com/en/article/5145691>

Download Persian Version:

<https://daneshyari.com/article/5145691>

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