ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–17

Available online at www.sciencedirect.com

ScienceDirect

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

Review Article

Recent progress in hydrogen production from formic acid decomposition

Xian Wang [a,b], *Qinglei Meng* [a,d], *Liqin Gao* [a,b,c], *Zhao Jin* [a], *Junjie Ge* [a,*], *Changpeng Liu* [a], *Wei Xing* [a,c,**]

[a] *Laboratory of Advanced Power Sources, Jilin Province Key Laboratory of Low Carbon Chemical Power Sources, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, PR China*

[b] *University of Chinese Academy of Sciences, Beijing, 100039, PR China*

[c] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, PR China*

[d] *University of Science and Technology of China, Hefei, Anhui, 230026, PR China*

ARTICLE INFO

Article history:
Received 13 December 2017
Received in revised form 20 February 2018
Accepted 22 February 2018
Available online xxx

Keywords:
Formic acid decomposition
Hydrogen production
Heterogeneous catalysis
Homogeneous catalysis
Catalysis selectivity

ABSTRACT

Formic acid, as the simplest carboxylic acid which can be obtained as an industrial by-product, is colorless, low toxicity, and easy to transport and storage at room temperature. Recently, Formic acid has aroused wide-spread interest as a promising material for hydrogen storage. Compared to other organic small molecules, the temperature for formic acid decomposition to produce hydrogen is lower, resulting in less CO toxicant species. Lots of catalysts on both homogeneous catalysts and heterogeneous were reported for the decomposition of formic acid to yield hydrogen and carbon dioxide at mild condition. In this paper, the recent development of mechanism and the material study for both homogeneous catalysts and heterogeneous catalysts are reviewed in detail.

Contents

* *Corresponding author.*
** *Corresponding author.* Laboratory of Advanced Power Sources, Jilin Province Key Laboratory of Low Carbon Chemical Power Sources, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, PR China.
E-mail addresses: gejj@ciac.ac.cn (J. Ge), xingwei@ciac.ac.cn (W. Xing).
https://doi.org/10.1016/j.ijhydene.2018.02.146

Please cite this article in press as: Wang X, et al., Recent progress in hydrogen production from formic acid decomposition, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.146

Introduction

Traditional fossil fuels are creating serious climate and environment issues globally [1–3]. Meanwhile, due to the increase in energy demand, the global fossil fuel consumptions rate is expected to double in the next thirty years, which makes their doomed depletion end come earlier. Therefore, taking advantage of sustainable energy resources, such as wind and solar energies, is imperative, and has received huge amount of attention [4,5]. The intermittent nature of solar and wind energies necessitates for energy storage media and technique for its efficient on demand release. Hydrogen is an ideal energy carrier with high energy density, cleanness, and earth abundance. The energy stored in the hydrogen molecule can be efficiently utilized through a variety of ways, among which proton exchange membrane fuel cell (PEMFC) is highly attractive due to its high energy efficiency, environmental benign and high energy density. There are many viable ways to product hydrogen, such as water electrolysis [6,7] (Equation (1)), hydrogenase route [8] (Equation (2)), and extraction from biomass such as methanol [9] and formic acid [10–12] (Equation (3)).

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)(\text{electrolysis}) \quad (1)$$

$$2H^+ + 2X_{\text{reduced}} \rightarrow H_2 + 2X_{\text{oxidised}}(\text{hydrogenase}) \quad (2)$$

$$HCOOH \leftrightarrow H_2 + CO_2(\text{homo/heterogeneous catalysis}) \quad (3)$$

Among these solutions, hydrogen production from formic acid (FA) is a promising route to store and release at room temperature, with the advantages of high gravimetric (4.4 wt %) and volumetric (53.4 g/L) H_2 capacity [12]. As the simplest carboxylic acid, FA is a colorless and low toxicity liquid at ambient condition (density = 1.22 g/mL, m.p. = 281.5 K, b.p. = 373.9 K), which can be obtained as an industrial by-product, through photoelectric catalytic CO_2 reduction, and by decomposition of biomass [13]. The liquid phase FA decomposition (FAD) to yield hydrogen has been realized, making the H_2 production at mild condition promising for the on demand release and utilization in hydrogen fuel cell vehicles. Selectivity is an important issue as it determines the quality of the final H_2 gas generated. Depending on the type of catalysts used and the working condition, such as reactant concentration and the reaction temperature, formic acid decomposition (FAD) may happen via the following two possible ways [14] (Scheme 1).

In reaction pathway 1, FA decomposes through dehydrogenation pathway and produces hydrogen and carbon dioxide, which is the reverse reaction process of carbon dioxide hydrogenation. Thus hydrogen can be effectively stored in formic acid through this cycle. At present, major efforts are concentrating on carbon dioxide hydrogenation [15], where several effective techniques have been developed. However, much fewer efforts have been paid on the FAD to produce hydrogen, which deserves more attention.

In this review, we will focus on the recent development of FAD catalysts on both homogeneous catalysts and heterogeneous catalysts. We will also give a summary on proposed future research direction for FAD along with possible obstacles on the formic acid hydrogen storage that may be encountered.

Homogeneous catalysts for formic acid decomposition

Over the past few decades, massive efforts were paid to search for high performance homogeneous catalysts towards FAD. In 1967, Coffey reported that soluble platinum, ruthenium and iridium phosphine complexes were efficient in selectively decomposing formic acid into H_2 and CO_2 [16]. Since then, massive research endeavors have been concentrated on the development of highly efficient noble-metal ruthenium and iridium complex. Meanwhile, catalysts based on non-noble metals complex such as iron and copper were occasionally reported [17–22].

Ruthenium-based catalysts

In 2000, Puddephatt and co-workers investigated the binuclear Ru complex for the dehydrogenation of FA [23]. The dissolved [Ru_2(μ-CO)(CO)$_4$(μ-dppm)$_2$] catalyst in acetone

$$HCOOH \rightleftharpoons CO_2 + H_2 \quad (1)$$

$$HCOOH \rightleftharpoons CO + H_2O \quad (2)$$

Scheme 1 – Possible ways for the formic acid decomposition.

Please cite this article in press as: Wang X, et al., Recent progress in hydrogen production from formic acid decomposition, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.146