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Full Length Article

Large volume *in situ* H_2 production on fixed bed reactor by concentrated formic acid aqueous solution

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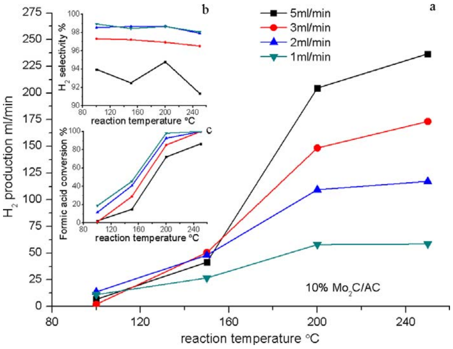
GRAPHICAL ABSTRACT



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ABSTRACT

Formic acid is a promising hydrogen storage material for its high H_2 capacity, easy transfer and moderate H_2 regeneration conditions. Active carbon supported Mo_2C with or without Co doping were used as the heterogeneous catalyst in the decomposition of a high concentrated aqueous solution of formic acid up to 50% on a fixed bed reactor. For a given flow rate and reaction temperature, though higher volume of H_2 is produced per unit time, the increase in formic acid's concentration reduces both H_2 selectivity and formic acid conversion rate. At 250 °C, a stream of 236 mL/min H_2 was generated continuously at a high H_2 selectivity (91%) and formic acid conversion rate (86%), from a 10% formic acid fed at the flow rate of 5 mL/min. High reaction temperature improved the conversion of formic acid feed at little expense of H_2 selectivity. The doping of Co in the Mo_2C lattice improves the H_2 selectivity to 100% at 100–200 °C. A life time study showed the stability of this system by the remained high H_2 selectivity in formic acid decomposition. This work of using active carbon supported molybdenum carbides and high concentrated aqueous formic acid, opens up a new route for the portable H_2 generator using formic acid as a hydrogen storage material at no environmental risk.

1. Introduction

Electric vehicles are considered as the green source powered vehicle due to the zero onsite carbon emission. The widely usage of electro automobiles is also the solution to reduce huge consumption of fossil energy and so caused environmental problems, since a quarter of the petroleum product is burned by vehicles each year. The fuel cell vehicles present apparent flexibility compared to plug-in electronic vehicles and the refilling system is similar to the existent gas station used worldwide. The current obstacle of large-scale application of fuel cell vehicle is the storage of hydrogen [1–4]. The costs of hydrogen storage and regeneration hinder the commercial application of fuel cell vehicles

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[5,6].

One of the most promising hydrogen storage is formic acid [7,8]. Pure formic acid stores 4.3 wt% hydrogen; the size of a formic acid tank containing energy capacity of 500 km's trip is similar to that of the currently used fuel tank, 40–50 L [9,10]. With formic acid as the hydrogen carrier, no great change is needed in the design of family cars and neither the current fuel refilling system, e.g. a petrol station.

Formic acid's decomposition follows two schemes. With appropriate catalysts, formic acid decomposed into CO and H_2O, or H_2 and CO_2 competitively [11,12]. The following aspects have to be considered to use formic acid as the portable hydrogen source. First, pure H_2 is the desired product, which requires high H_2 selectivity of the catalysts; Second, a continuous production of H_2 is favorable, this suits a heterogeneous system [13,14]; Third, the H_2 output is adjustable and adequate; this requires a high conversion of formic acid and quick response [15]; Finally, to ensure the environmental safety, there are no additional chemical involved in the system, namely no addition of acid, base nor any organic solvents. The main challenge is the development of catalysts to fulfill all these respects [16–18].

The development of heterogeneous catalysts with high H_2 selectivity and activity could be one solution. Many attempts have been made to decompose formic acid on heterogeneous catalysts, especially with precious metal and alloys. Chan and coworkers found that the addition of bismuth oxide improved the catalytic abilities of both mono- or di- nuclear Pt and Ru oxides in hydrogen generation from aqueous formic acid/ formate solution at near ambient temperature, though the conversion of formic acid and production of H_2 require improvements [19–21]. Their work with Pd/C system presents a higher H_2 production rate at an elevated temperature [22].

Work from Xing and coworkers found that the addition of CeO_2 promoted the catalyst abilities of Pd-Au/C and Pd-Ag/C alloys in aqueous formic acid/ formate solution greatly; at 365 K, the lifetime has reached 240 h [23]. Their later work found that by doping rare earth elements or forming core-shell structures, the catalytic abilities of Pd-Au/C were greatly promoted in formic acid decomposition [24,25]. Core-shell particles formed purely by precious metal Ag and Pd presented 100% H_2 selectivity below 50 °C. The conversion rate of aqueous formic acid is improved at 70 °C and above at the cost of H_2 selectivity and CO was detected in the tail gas [14]. The promotion effects of boron in Pd/C catalyzed formic acid decomposition [26] is recently reported. Modification of support materials also improves the reactivity of Pd catalysts [27].

Gas phase formic acid were fully decomposed at elevated temperatures on Pd/C, with only trace of CO detected, as presented in the work of Ross and Solymosi's groups and others [28–32]. In their later work, Ross and coworkers found the addition of K to Pd/C systems improves the activity of formic acid's decomposition at a lower reaction temperature [33,34]. Properly dispersed Au systems also performs high reactivity in formic acid's decomposition. Iglesia and coworkers found that highly dispersed Au loaded Al_2O_3 catalysts presented higher H_2 selectivity compared to that of Pt loaded Al_2O_3 in formic acid's decomposition with He as carrier gas at near–ambient temperatures [35,36].

Apart from their work with precious metals as the reactive species, Solumosi and coworkers also tested formic acid's decomposition on active carbon and Norit supported molybdenum carbide. A full formic acid conversion and 100% H_2 selectivity was achieved with this gas phase reaction with He as the carrier gas at 200 °C [37]. Some non-precious, non-transition metal salts, such as sodium germanate presents reasonable activity towards formic acid's decomposition, at elevated temperatures [38].

Apart from the conventional heterogeneous catalysts, nano particles of precious metal and alloys are widely studied in the decomposition of formic acid especially in the past few years. Ross and coworkers found the N-doped Pt nano-particles present high CO tolerance and the H_2 selectivity remains over 99% [39]. Both support free and supported Pd/Ag nanoparticles are used in the catalyzed formic acid decomposition; supports used including TiO_2, MOFs, SiO_2 etc [40–44]. The bimetallic Ag-Pd core-cell particles present a H_2 selectivity of nearly 100% in the decomposition reaction of 1 M aqueous formic acid [14]. Mori and coworkers observed promotion effects of amino groups in the supported resins, resulting in a higher formic acid conversion on nano particles composed of Pd or its alloy with Ag or Cu [45–47]. The addition of MnO_x improves the tolerance of CO and reduces leaching and agglomeration of Pd or Ag/Pd alloy nano particles [48,49]. Mono-dispersed Au and Pd particles on carbon support present a high H_2 selectivity of 100% [50]. The Au-Pd alloy synthesized by reduction with the assistance of Mg^{2+} presents higher activity of formic acid decomposition on carbon supports, though CO was detected in the tail gas [51].

In reaching a general application of formic acid based energy source, researches focused on catalyst activity optimization are essential but not merely. To operate formic acid decomposition on demand in a continuous reaction mode, pioneering works by Laurenczy and Bellers made construction of fittings first with round bottom flask then improved to autoclave with homogenous catalysts [11,15,52,53]. Attempts of immobilization or solidify of homogenous catalyst could also be a solution to provide a continuous hydrogen flow [54]. Fixed-bed reactors were used mainly in the a gas phase reaction with Ar or He as carrier gas [13,19,29,30,33,37–39,55], few reports were in liquid phase [20,32,48,49].

Herein, we use active carbon supported Mo_2C (brief as Mo_2C/AC) catalysts in the decomposition of formic acid. The formic acid aqueous solution was introduced into the fixed-bed reactor with no other additives. The amount of hydrogen generated from the reactor is adjustable by alternating the flow rate and concentration of the formic acid solution. High concentrated aqueous formic acid solution (up to 50%) was tested as feed stock. The heterogeneous Mo_2C/AC presents high H_2 selectivity and formic acid conversion; the maximum volume of hydrogen obtained by 15 mL of catalyst reached 236 mL/min, at high H_2 selectivity (91%) and formic acid conversion rate (86%). The doping of Co in Mo_2C reforms the Mo_2C crystals, which improves the H_2 selectivity to 100% at 100–200 °C with little expense of formic acid conversion. Though low concentrated formic acid is applicable for the portable H_2 generator, the higher concentrated formic acid produces larger volume of H_2 per unit time. In this work we studied the reaction temperature, flow rate and concentration of formic acid to optimize the active window of Mo_2C/ active carbon.

2. Experiment

2.1. Catalyst synthesis and characterization

Heterogeneous Mo_2C/AC catalysts with or without doping at the theoretical Mo_2C loading of 1%, 2% and 10% in weight, were prepared by calcination of certain precursors under N_2 [56]. Ammonium molybdate dissolved in water and 1,8-Diaminonaphthale or 1,5-Diaminonaphthale, dissolved in ethanol as the carbon source were loaded on active carbon (from Aladdin, meshed 8–14, washed with 1% HCl aqueous solution and water before use) support by impregnation. The precursor obtained were calcined under N_2 at 750 °C for 6–8 h. The catalyst was used with no further purification. Powder X-ray diffraction patterns were recorded on a Rigaku SmartLab 9 kW diffractometer equipped with a Cu-Ka1 radiation (Ge-monochromated, $\lambda = 1.54,056$ Å) in the 2θ range of 10–80° with a scan speed of 4°/min. The scanning electron microscope images of the catalysts were taken on a LEO-1530VP field-emission scanning electron microscope. The N_2 adsorption/desorption measurements were performed at 77 K on a Micromeritics ASAP 2020 instrument. The samples were all outgassed at 200 °C for 3 h before measurement.