



Non-precious molybdenum-based catalyst derived from biomass: CO-free hydrogen production from formic acid at low temperature

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ABSTRACT

CO-free hydrogen was successfully produced from the dehydrogenation of formic acid at a temperature near its boiling point of 110 °C by using a high-performance non-precious metal molybdenum based catalyst synthesized from soybean and earth-abundant molybdenum. The effect of carbonization temperature, raw material ratio on the catalytic activity for formic acid decomposition were investigated in details. The catalyst Soy-Mo (0.1) prepared at a carbonization temperature of 750 °C, the weight ratio of the soybean powder to Mo precursor of 1:0.1 showed the best catalytic activity among those as-synthesized catalysts. Even at a temperature as low as 110 °C, HCOOH conversion reached above 80% with a 100% H₂ selectivity and a long-term stability. It indicated that the catalysts derived from those biomass enriched in protein and alkaline metals have excellent performance for catalytic formic acid decomposition. This approach provided a new path for design and development of catalysts with high performance for CO-free hydrogen generation from formic acid in a large-scale industrial process.

1. Introduction

Hydrogen is considered as a clean and highly abundant fuel, however, the storage and transport limit its large-scale applications in our daily life [1–3]. Hydrogen release from hydrogen storage chemicals is an effective way to get hydrogen on-site. Formic acid (HCOOH), as a promising H₂ storage chemical with high energy density and excellent stability at room temperature, has recently received extensive attention [4–6]. H₂ can be generated by catalytic decomposition of formic acid with byproducts of CO₂ and/or CO. In this process, CO generation should be avoided because it is a poison gas for Pt-based electrode in fuel cell even with a trace amount [7,8]. Therefore, as one of the main goals of hydrogen production for fuel cells applications, CO-free hydrogen production from the decomposition of HCOOH is necessary. In the past decades, various suitable catalysts for CO-free hydrogen production from HCOOH have been developed [5,7]. Many of them with excellent performance at near ambient temperatures belong to homogeneous catalysts, mainly metal complex-based homogeneous catalysts [9–11]. However, the difficulty in the separation of catalysts from the reaction mixture limits their large-scale applications. In addition, the

need of additional organic solvents in the formic acid decomposition results in the process costly, complicatedly and always toxically. As such, heterogeneous catalysts have been paid considerable attention in recent years due to its superiorities on controlling, recycling and easy separation. In the developing catalysts, noble metal based catalyst such as Au/ZrO₂ [12], Pd/CeO₂ [13], Pd-Pt [14], Pd-Au/C [15,16], PdNiAg [17], CoAuPd [18], AgPd@Pd [19], AgPd@ZIF-8 [20] and AgPd@MOF [21] exhibited high performance. However, the scarcity and high cost of such noble metal based catalysts also limited their large-scale industrial applications. Thus, the development of non-precious metal heterogeneous catalysts with high performance for hydrogen generation from formic acid at low temperatures is required.

To date, only a few no-precious-metal heterogeneous catalysts were reported and they also showed substantially lower activity even at high temperatures [22–24]. Halawy et al. [25] investigated the gas-phase formic acid decomposition over α -Fe₂O₃ at 200 °C and found that the maximum of formic acid conversion was only 24.1%. Patemarakis [26] conducted the formic acid decomposition over pure γ -Al₂O₃ and doped (+MgO (1% w/w)) γ -Al₂O₃ at 275–400 °C and found that at 400 °C, the H₂ selectivity was only 20% over pure γ -Al₂O₃, however, by doping

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Mg^{2+} , the H_2 selectivity reached about 60%. Koroteev et al. [27] studied the HCOOH decomposition over MoS_2 /graphene flakes and found that formic acid conversion reached 100% with 49% H_2 selectivity at 250 °C. Molybdenum carbide has been attracted great interest due to their noble metal-like catalytic activity in many important reactions, such as hydrogen evolution from electrolysis of water [28,29], water gas shift (WGS) [30], hydrocarbon isomerization [31], steam reforming of methanol (SRM) [32,33], methanol decomposition [34], methane reforming [35,36] and formic acid decomposition [22,23]. Flaherty et al. [23] studied the formic acid decomposition over C–Mo (1 1 0) surface and found that the H_2 selectivity over C–Mo (1 1 0) catalyst was significantly higher than the pure Mo (1 1 0) surface at all temperatures (77–427 °C). Especially, at lower temperatures 77–177 °C, C–Mo (1 1 0) showed 15 times higher selectivity towards formation than pure Mo (1 1 0), in which the C–Mo (1 1 0) selectively dehydrogenated ~70–75% of the formic acid but Mo (1 1 0) only dehydrogenated ~5%. In our previous studies [37], the morphology-controllable molybdenum carbides were synthesized and applied for FA decomposition at 100–350 °C, the relationship between organic carbon source structure and corresponding molybdenum carbide morphology were obtained and we also found that the catalyst with nanosheet structure prepared by using 4-Chloro-*o*-phenylenediamine (4CloPd) as the carbon source showed the highest FA conversion of near 100% with a low CO selectivity when the reaction temperature was higher than 250 °C. Following, its catalytic performance was further improved by doping with various metal nanoparticles (Ni, Co, Mg, Cu and Ag) [38]. It is found that Ag and Mg doped Mo_xC_y catalysts exhibited much higher catalytic activity than others and $\text{Mg}_{1.0}\text{Mo}_{9.0}\text{C}_{1-x}$ had the highest formic acid decomposition performance with a high conversion (above 90% at 200 °C), a low CO production (< 10% at 200 °C) and a long-term stability.

The molybdenum-based catalyst which contain molybdenum carbide and molybdenum nitride simultaneously shows higher activity for many important reactions than the molybdenum carbide catalyst [39,40]. These findings encourage us to use this type of catalyst for formic acid decomposition. In order to further improve the catalytic performance of molybdenum-based catalysts for formic acid decomposition, in this work, the molybdenum-based catalysts were synthesized by using soybean which rich in protein as carbon source and nitrogen source. The effect of carbonization temperature, raw material ratio on the catalytic activity for formic acid decomposition were investigated in details. It is expected that CO-free hydrogen production from the decomposition of formic acid can be achieved at low temperature. These findings could provide a new idea for designing and developing non-precious heterogeneous catalyst for formic acid decomposition in industrial application of formic acid based hydrogen storage.

2. Experimental

2.1. Catalysts preparation

Molybdenum-based catalysts with various raw material ratios at different carbonization temperatures were prepared as reported by Chen et al. [40]. The soybean (produced in Hokkaido, Japan) was pulverized and sieved into < 0.075 mm (200 mesh) of particle size using a stainless steel sieve. Grounded soybean powder was added in ammonium heptamolybdate (AHM, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Kojundo Chemical Laboratory Co., 99%) aqueous solution under stirring at room temperature, and then treated in ultrasonic bath for 60 min to form a homogenous suspension. Subsequently, the mixture were dried at 90 °C in an oven overnight. Herein, the raw material weight ratio of soybean to Mo sources (AHM) were 1:0.025, 1:0.05, 1:0.1, 1:0.14, 1:0.2 and 1:1, respectively. Thereafter, the carbonization of the dried precursors was carried out in a fixed-bed quartz micro-reactor with an inner diameter of 10 mm. Here, high-purity Ar with a flow rate of 50 cm^3/min was used

as the carrier gas to provide an inert atmosphere. Before carbonization, the reactor was purged with Ar (50 cm^3/min) at room temperature for 4 h to remove out any remained air. Then, the sample was heated to final carbonization temperature (i.e., 650, 750, 800 and 850 °C, respectively) with a heating rate of 5 °C/min and maintained at the final temperature for 2 h. Finally, the catalysts were passivated in 1% O_2/Ar at room temperature overnight. As a result, a black catalyst powder was obtained. Herein, the catalysts with soybean/AHM weight ratios of 1:0.025, 1:0.05, 1:0.1, 1:0.14, 1:0.2 and 1:1 are denoted as Soy-Mo (0.025), Soy-Mo (0.05), Soy-Mo (0.1), Soy-Mo (0.14), Soy-Mo (0.2) and Soy-Mo (1), respectively. In addition, the Soy-Mo (0) was also synthesized using the similar procedure, where only pure soybean powder was dissolved in distilled water in the preparation of the catalyst precursor without AHM. Herein, the catalysts prepared at different carbonization temperatures are denoted as Soy-Mo-650, Soy-Mo-750, Soy-Mo-800 and Soy-Mo-850, respectively.

For comparison, the molybdenum-based catalysts derived from apple tree branch (ATB) with ATB/Mo weight ratio of 1:0.1 was also prepared by using the same method. This catalyst is denoted as ATB-Mo (0.1).

2.2. Catalyst characterization

X-ray powder diffraction (XRD) analysis was conducted by using Rigaku Smartlab XRD analyzer (Japan) using $\text{Cu K}\alpha$ as radiation with an operating potential of 30 kV, a current of 30 mA and a scanning rate of 4°/min. Particle surface morphology and microstructure of the samples were characterized using a scanning electron microscope (SEM, SU8010, Hitachi, Japan) coupled with energy dispersive spectrometer (EDS) and transmission electron microscope (TEM, JEM-2100F, JEOL). The elemental composition (C, H, N, S and O) of pure soybean as well as the catalysts were analyzed by using an elemental analyzer (Vario EL cube elemental analyzer). The basicity of catalyst was investigated by CO_2 -Temperature-programmed desorption (CO_2 -TPD) using a BEL-CAT catalyst analyzer (BEL, Japan) equipped with a thermal conductivity detector (TCD). In a typical measurement, the catalyst was charged in a U-shaped quartz cell and preheated under helium flow at 500 °C for 1 h in order to remove out moisture and some impurities within the catalyst structure. Then, the preheated catalyst was saturated with a gas mixture of 5% $\text{CO}_2/95\%$ He with a flow rate of 50 cm^3/min at ambient temperature for 1 h. After stabilization, CO_2 desorption was performed from room temperature to 600 °C with a heating rate of 10 °C/min under He flow. Here, the CO_2 -desorption peak was detected using a TCD and the adsorbed CO_2 concentration was quantified from the peak area by calibrating using the standard gas. X-ray photoelectron spectroscopy (XPS) analysis was done with an AXIS ULTRA DLD spectrometer, using Al $\text{K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) as the photo source, generation at 150 W.

2.3. Catalyst activity evaluation

Catalytic performance was evaluated in a micro-reactor with an inner diameter of 6 mm. Schematic illustration of the formic acid decomposition reaction setup can be found in our pervious study [37]. Prior to the reaction, the catalyst was activated with 15% CH_4/H_2 at 590 °C for 2 h to reduce the oxide layer on the catalytic surface, the same as used in our previous work [41,42]. Formic acid decomposition was conducted at 100–150 °C as well as atmospheric pressure. Herein, formic acid was injected into the reactor by a syringe pump at certain feeding rate. It was pre-vaporized with a heater at 110 °C and carried by Ar gas with a flow rate of 50 cm^3/min to the reactor. 0.25 g of the catalyst was used in this study. A thermocouple was inserted into the reactor to control the reaction temperature, and two water-ice cold traps were set at the exit of the reactor. The gas products were analyzed using a gas chromatograph (GC) with TCD detector (Agilent 7890A GC system). A FID-GC (Shimadzu 2014 GC system) was used to ensure no

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