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Low Temperature H_2 Production from Formic Acid Aqueous Solution Catalyzed on Metal Doped Mo_2C

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Abstract: Hydrogen is recognized as a promising energy scours in the close future. Online hydrogen preparation from formic acid under mild reaction conditions causes extensive interests. Mo_2C and metal (Fe, Ni, Co, K) doped Mo_2C on granular activated carbon (GAC) were prepared and used as heterogeneous catalysts for H_2 generation from formic acid on a fixed bed reactor at 100–250°C. The formic acid conversions on doped Mo_2C-Me/GAC are clearly improved, especially at lower reaction temperatures. Co doping presents outstanding effect on H_2 selectivity and conversion rate compared to Ni and Fe. A 56.3% formic acid conversion was reached on Mo_2C-Co/GAC at 100°C, which triples that on Mo_2C/GAC at the same temperature. At 150°C, a high formic acid conversion over 90% was reached on Mo_2C-Co/GAC. These long lifetime catalysts with no precious metal provide a low cost route to hydrogen production from formic acid.

Keywords: Hydrogen production; energy storage and conversion; Mo_2C/GAC; metal doping; formic acid decomposition; carbon materials

1 Introduction

At present, fossil fuels are still the main energy source worldwide. The use of fossil fuels leads to NO_X, SO_X and other air pollution, posing serious challenges to human survival. As a sustainable and environment friendly energy source, hydrogen has attracted more attention in recent years [1]. Though liquid phase hydrogen storage is applicable at present, compressed hydrogen storage remains a potential flammable and explosive security danger [1]. In addition to the high pressure technique, hydrogen storage techniques such as carbon nanotubes, glass microspheres and metal hydride are inefficient and still in laboratory stage [2–6].

Online hydrogen productions from liquid fuel such as formic acid, methanol and ethanol overcome the hydrogen storage problems effectively [7–10]. Though a high methanol conversion is achieved in the steam reforming reaction, the CO content in the rear gas prevents the direct application of this process in hydrogen fuel cells [1,11]. The CO production from ethanol steam reforming reaction is also high which is not conducive for fuel cell application. It is necessary to find suitable raw materials for online hydrogen production [10].

Formic acid, with the advantages of mild reaction conditions and wide availability, is a promising material for hydrogen production [10]. Both homogeneous and heterogeneous catalysts in hydrogen production from formic acid are extensively studied worldwide. Homogeneous catalysts are highly active and selective. Most homogeneous catalysts are Ru contained, including [$RuCl_2(PPh_3)_3$], [{$RuCl_2$ (benzene)}$_2$], $RuCl_2$(p-cymene)$_2$ and $RuBr_3 \cdot xH_2O$ [12–14]. The activity and stability of these catalysts vary significantly with the proportion of amine, acid, concentration and type of ligands [15].

The study of hydrogen production from formic acid decomposition on heterogeneous catalysts began since the 1930s. Various precious metal, copper and nickel catalysts were reported in the literature. The research is mainly focus on improving the catalyst activity and hydrogen selectivity [16–18]. The formic acid decomposition are highly active on single or few atomic Au particles [16,17]. Gold nanoparticles on Al_2O_3 prepared by Ojeda et al. present high catalytic activity with a near 100% H_2 selectivity. Huang et al. prepared novel core-shell structured heterogeneous PdAu@Au/C catalyst with higher activity, selectivity at low temperature [17].

Molybdenum carbide (Mo_2C) presents excellent performance, high stability and high H_2 production from formic acid in both liquid and gas phase [19,20]. Our previous study showed that Mo_2C contained 0.6 wt% Co presented a 100% H_2 selectivity in H_2 generation from formic acid decomposition [21]. Though not widely studied on Mo_2C system, research show the promotion effects of transition metals in Mo contained catalyst. Transition metal doped MoS_2 presents high activities in hydrodesulfurization, hydrogen generation and oxygen reduction in fuel cells [22–24]. Synergetic effects were used to explain these promotion [25]. Botalla and coworkers found that K doped Mo–V–Sb–O catalysts show high activity and selectivity in acrylic acid preparation from propane oxidation [26]. To obtained durable and low cost catalysts with high activity and selectivity in H_2 production from formic acid at ambient or near ambient temperature is crucial in the application of this process in portable H_2 generation.

In this work, we studied the preparation of metal doped Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) catalysts and the performance of these catalysts in the hydrogen production from formic acid decomposition. Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) catalysts were prepared by impregnation with granular activated carbon (GAC) as carrier. Results show that Mo_2C-Me/GAC (Me = Fe, Ni, Co) catalysts presented high activity in formic acid decomposition and high H_2 selectivity especially at low temperature compared to Mo_2C/GAC, among which Co doped catalyst shows the best performance. At 150°C, Mo_2C-Co/GAC presents a 99.7% H_2 selectivity and 91.6% formic acid conversion, which are both higher compared to none doped Mo_2C/GAC. Alkalis metal K in Mo_2C/GAC improves the conversion rate of formic acid, but reduces H_2 selectivity.

2 Experiment

All chemicals including 1,8-Diaminonaphthale, ammonium molybdate, ethanol, HCl, GAC, $Fe(NO_3)_2 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and KNO_3 were purchased from Sinopharm group chemical reagent Co., Ltd. Formic acid was purchased from Shanghai Lingfeng chemical reagent Co., Ltd.

X-ray diffraction pattern (XRD) was obtained with a Rigaku SmartLab 9 kW diffractometer equipped with a Cu-Kα radiation (Ge-monochromated, $\lambda = 1.54056$ Å) in the 2θ range of 10–80° with a scan speed of 4°/min. The fixed bed reactor used in the catalytic activity evaluation was home made. A gas chromatography (SHIMADZUGC2014) with a tubular furnace (Tianjin Zhonghuan experimental electric furnace Co., Ltd) was used in the detection of the rear gas. 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 out gassed at 200°C for 3 h before measurement.

The GAC carrier (meshed 8–14) was pretreated with boiling hydrochloric acid solution (10%) for 15 min. It was then washed with distilled water at 100°C for 12 hours to pH = 7 before use. To prepared 10% Mo_2C loaded Mo_2C-GAC, ammonium molybdate (1.3 g, 6.6 mmol) dissolved in water and 1,8-Diaminonaphthale (1.3 g, 8.2 mmol) dissolved in ethanol were adsorbed on 6.7 g of GAC, respectively. Then 0.33 mmol of $Fe(NO_3)_2·9H_2O$, $Ni(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$ or KNO_3 was dissolved in deionized water and adsorbed on the active carbon carrier, the obtained product were dried at 80°C overnight. The precursor obtained were calcined under N_2 at 750°C for 6–8 h to obtain Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) catalysts. The obtained catalysts were then filled in a fixed bed reactor and evaluated in H_2 generation from formic acid decomposition.

3 Results and Discussions

Mo_2C phase are successfully synthesized and dispersed on porous GAC, which is presented by XRD and SEM studies. The XRD pattern of the synthesized Mo_2C loaded GAC catalysts are presented in Fig. 1a. Typical diffraction peaks of Mo_2C (JCPDS NO. 72-1683) at 2θ = 34.4°, 38, 39.5°, 52°, 61.8°, 69°, 73°, 76° are observed as the main phase in all the doped Mo_2C-Me/GAC catalysts. A small amount of Co and CoO phase are observed in the Co doped Mo_2C-Co/GAC. Ni metal phase is detected in the Ni

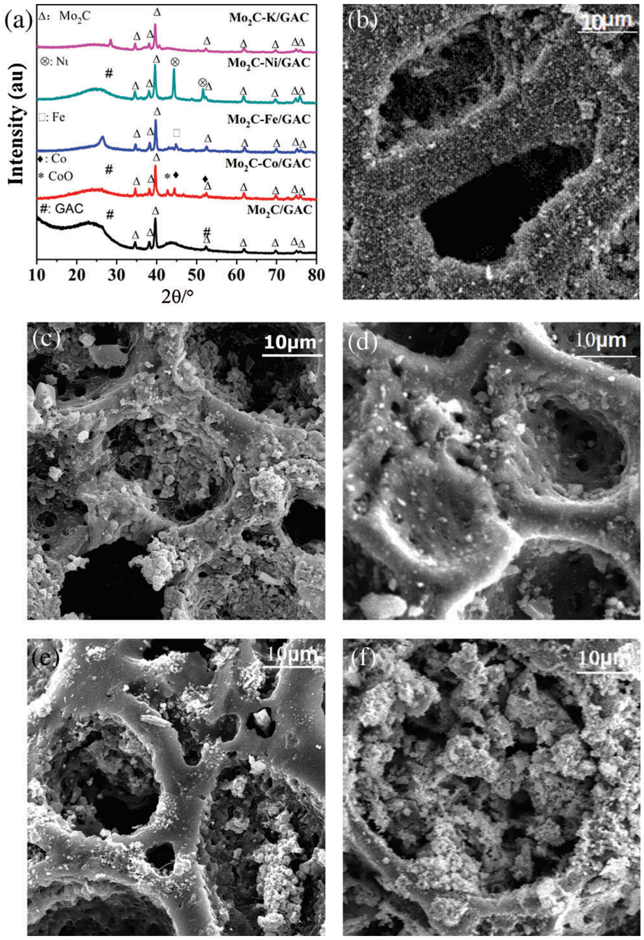

Figure 1: a) XRD patterns of Mo_2C/GAC and Mo_2C-Me/GAC (Me = Fe, Ni, Co, K). SEM images of Mo_2C/GAC and Mo_2C-Me/GAC catalysts: b) Mo_2C/GAC; c) Mo_2C-Co/GAC; d) Mo_2C-K/GAC; e) Mo_2C-Fe/GAC and f) Mo_2C-Ni/GAC

doped Mo_2C-Ni/GAC. No significant difference was detected in the grain size of Mo_2C/GAC and doped Mo_2C-Me/GAC catalysts. The typical XRD patterns of GAC are also presented.

The SEM images of Mo_2C/GAC and Mo_2C-Me/GAC catalysts demonstrate evenly dispersed Mo_2C particles on GAC surface and channels. Large particles of Mo_2C on GAC were obtained by metal doping compared to Mo_2C/GAC. The specific surface area measurements, Tab. 1 of the synthesized Mo_2C-Me/GAC are increased slightly by Ni, Fe, Co and K doping compared to none-doped Mo_2C/GAC. Mo_2C-Co/GAC presents the highest specific areas among these catalysts.

Table 1: Specific surface area of Mo_2C-Me/GAC and Mo_2C/GAC

Catalysts	*SBET*/($m^2 \cdot g^{-1}$)
Mo_2C/GAC	502.9
Mo_2C-Ni/GAC	535.1
Mo_2C-Fe/GAC	596.1
Mo_2C-K/GAC	582.5
Mo_2C-Co/GAC	599.9

Mo_2C/GAC and Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) catalysts, 15 ml (≈6.7 g) were filled in the fixed bed reactor and heated up to 270°C under 5% of H_2/Ar for 2 h. The pretreated catalysts were then cooled to room temperature under pure N_2. A 10% formic acid aqueous solution was filled in the reactor at a follow rate of 1 ml/min. The rear gas was cooled to room temperature and the gas and liquid phase were collected separately. CO and CO_2 in the gas product were analyzed by SHIMADZU GC2014 gas chromatograph equipped with a TDX01 chromatographic column and a TCD detector. The formic acid concentration in the feed and liquid rear products were detected by SHIMADZU GC2014 on a GDX103 chromatographic column with a TCD detector. The formic acid decomposition reaction was carried out at 100°C, 150°C, 200°C and 250°C on the fixed bed reactor. The formic acid decomposition rate and H_2 electivity on 15 ml of prewashed and dried GAC were also tested under the same condition as Mo_2C/GAC and Mo_2C-Me/GAC, for comparison. No activity was observed on pure GAC. Catalytic performance of hydrogen production from formic acid decomposition at various temperature on 15 ml of Ni, Fe, K and Co doped Mo_2C-Me/AC are presented in Tab. 2.

The H_2 selectivity of the prepared catalysts was calculated as the quotient of the amount of CO_2 detected and the sum of CO and CO_2. The conversion rate was calculated as the quotient of the difference of the formic acid concentration of the feed and remainder and the feed.

The formic acid conversion and H_2 selectivity against the reaction temperature are demonstrated in Figs. 2a and 2b. All Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) catalysts present higher formic acid conversation rate compared to the none-doped Mo_2C/GAC. The formic acid decomposition rate are highly improved on Mo_2C-Me/GAC (Me = Fe, Ni, Co, K) at lower reaction temperature. This is agreed with the reported enhancement of methanol dissociative adsorption on Cu modified Mo_2C catalysts, which is associated with the activity at low temperatures compared to pure Mo_2C [27]. A 56.3% formic acid conversion was reached on Mo_2C-Co/GAC at 100°C, which triples that on Mo_2C/GAC at the same temperature. At 150°C, a high formic acid conversion over 90% was reached on Mo_2C-Co/GAC. K doped Mo_2C-K/GAC also presents high formic acid conversion at 150°C. One hundred percent formic acid at 200°C was reached on Mo_2C-Co/GAC and Mo_2C-K/GAC. At 250°C all catalysts present 100% formic acid conversion rate.

All the catalysts used presents high H_2 selectivity over 90% against CO in H_2 production from formic acid decomposition. H_2 selectivity of all catalysts decreased as the reaction temperature increases. H_2

Table 2: Catalytic performance of hydrogen production from formic acid decomposition at various temperatures on 15 ml of 0.5% Ni, Fe, K and Co doped Mo_2C/AC with a formic acid aqueous solution feeding rate of 1 ml/min

Catalysts			Reaction temperature /°C	Conversion /%	H_2 Selectivity /%
	Mo_2C	Dopant			
Mo_2C/AC	10%	0	100	18.9	98.9
			150	45.5	98.4
			200	98.2	98.7
			250	100	98.1
Mo_2C-Ni/AC	10%	Ni 0.5%	100	25.2	99.5
			150	48.6	99.4
			200	98.9	99.3
			250	100	98.2
Mo_2C-Fe/AC	10%	Fe 0.5%	100	25.2	99.7
			150	55.3	99.6
			200	98.7	99.4
			250	100	98.5
Mo_2C-K/AC	10%	K 0.5%	100	32.8	96.9
			150	73.6	96.7
			200	100	96.0
			250	100	93.4
Mo_2C-Co/AC	10%	Co 0.5%	100	56.3	99.9
			150	91.6	99.7
			200	100	99.6
			250	100	99.0

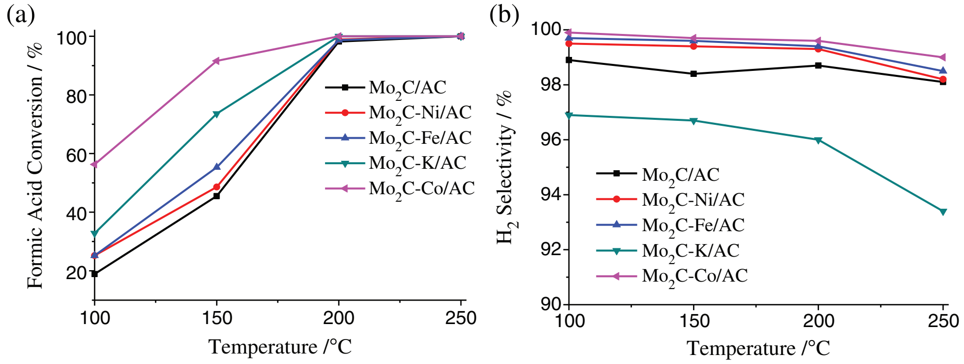

Figure 2: Effects of metal doping on hydrogen production from 10% formic acid aqueous solution decomposition at 100°C, 150°C, 200°C, 250°C with a flow rate of 1 ml/min: a) Formic acid conversion on Mo_2C-Me/GAC (Me = Fe, Ni, Co, K); b) Hydrogen selectivity on Mo_2C-Me/GAC (Me = Fe, Ni, Co, K)

selectivity improved by metal doping in Mo_2C-Co/GAC, Mo_2C-Ni/GAC and Mo_2C-Fe/GAC compared to none-doped Mo_2C/GAC. The synergetic effects of transition metal on Mo_2C are clearly observed in the Mo_2C-GAC materials, which improve both the activity and selectivity towards H_2 [28]. Though K doped Mo_2C-K/GAC presents higher formic acid conversion compared to none dope Mo_2C/GAC, the H_2 selectivity of Mo_2C-K/GAC is the lowest among all the catalysts studied. The modification of the local Brønsted acid environment in Mo_2C-K/GAC leads to a high absorption of formic acid on the surface, and encourage the unfavorite side reaction to produce CO and H_2O [26]. A life time study of Mo_2C-Co/GAC at 100°C for 3 weeks was carried out, which declines the activities to around 67% of originate. The activity remained at that level from the second week till the end of the lifetime study and similar selectivity towards H_2 production remained, which is consistent with our previous work [21].

4 Conclusion

Metal doped Mo_2C-Me/GAC catalysts were prepared with the advantages of low cost, mild reaction conditions, high catalytic activity and hydrogen selectivity. Both the hydrogen selectivity and formic acid decomposition rate were improved on transition metal Fe, Ni and Co doped Mo_2C-Me/GAC catalysts. The formic acid conversion rate is highly improved at low reaction temperature. Mo_2C-Co/GAC presents the highest H_2 selectivity of 99.7% and formic acid conversion rate of 91.6% at 150°C among all the Mo_2C-Me/GAC catalysts. The formic acid conversion on Mo_2C-Co/GAC doubles that on Mo_2C/GAC at 150°C. Alkali metal K doping in Mo_2C/GAC promotes the conversion rate of formic acid, but reduces the selectivity of H_2. The specific surface areas of metal doped Mo_2C-Me/GAC catalysts were all increased compared to Mo_2C/GAC. A new way is provided in hydrogen production using formic acid as raw material, which is conducive to reducing environmental pollution and in line with the concept of sustainable development. Our catalysts screening process in searching of a proper none-noble candidate for H_2 production from formic acid decomposition was carried out on a home-made fix bed reactor at a lab scale test. Catalysts prepared from different batch production were used and the catalytic activity and selectivity remain at the similar high level. Plat design and full parameter control, including quantitative description of reaction data on the most promising catalyst in H_2 production from formic acid ought to be carried out in larger scales for potential industrial applications. Although the cost of the new non-noble metal catalyst is much lower, the preparation process is relatively complex and the catalytic mechanism of these catalysts was not thoroughly studied. Further work is needed to, so as to provide a clearer theoretical basis for design and preparation of a more efficient catalyst system.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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