

N- or S-doped porous carbon-based metal catalysts for hydrogenation of CO₂ to formic acid

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Abstract. Hydrogenation of CO₂ to formic acid (FA) is a promising method to meet the increasing energy demand and reduce CO₂ emissions. In this work, efficient catalyst was successfully designed and synthesized by loading uniformly dispersed Ir nanoparticles on N- or S-doped carbon materials, catalyzing the hydrogenation of CO₂ to FA. The experimental results showed that the catalytic performance of N-doped Ir/NC catalyst was much higher than that of S-doped Ir/SN catalyst. Ir/NC catalyst exhibited a high catalytic performance under the reaction conditions of 120 °C, 8 h and 6 MPa with a turnover number (TON) of 987. Moreover, a high TON of 3901 was achieved after 48h, thus indicating the good stability of the obtained catalyst.

Keywords: carbon-based metal catalyst; CO₂ hydrogenation; liquid organic hydrogen storage, formic acid, metal-support interaction.

1. Introduction

The continuous exploitation and consumption of fossil resources have led to an increase in CO₂ emissions and a depletion of resources [1]. Undoubtedly, the development of clean energy represents a highly effective approach to mitigating CO₂ emissions and reducing reliance on fossil fuels. Hydrogen energy is a promising way, but the use of H₂ is often limited by the storage methods [2]. Formic acid (FA) has the characteristics of being liquid at room temperature and ambient pressure, which is stable and convenient for transport and store. Moreover, FA has a high hydrogen storage content (w = 4.4%, 53 g/L), which is regarded as a potential chemical hydrogen storage material [3]. In addition, FA is one of the basic organic chemical raw materials, widely used in pesticide, medicine and other industrial fields. Therefore, CO₂ hydrogenation to FA can not only achieve large-scale storage and transportation of H₂, but also achieve the capture and reuse of CO₂, which is a green and sustainable carbon neutral reaction [4].

Because most of the reaction of CO₂ hydrogenation to FA needs to be carried out under high temperature and pressure conditions, highly stable catalyst is more demanding [5]. Therefore, heterogeneous catalysts with good stability and catalytic activity have attracted attention, and they can realize the separation and reuse of catalysts, reduce the cost of the catalytic process and protect the environment, which lead to heterogeneous catalysts more suitable for practical applications [6]. Carbon-based materials with stable structure, high specific surface area, ultra-high stability, and controllable surface chemistry have become widely used carrier materials [7]. At present, the preparation of catalysts by anchoring metal active sites on various carbon materials is a common method. Meanwhile, based on metal-support interaction (MSI), the electronic structure of the carbon material, the Lewis acid base on the catalyst surface and the Fermi level can be adjusted by loading different metals or heteroatom (N, S, P) doping methods, so as to effectively improve the activity and selectivity of the catalyst [5,8].

Here, elemental doped carbon materials, NC and SC, were successfully prepared by carbonizing small molecular metal complexes, in which 1,10-phenanthroline and 2,2-dithiophene were used as N and S sources, respectively (Fig. 1). Then, a series of carbon-based nanoparticles catalysts (M/NC or M/SC) were successfully prepared by wet chemical method using metal ion solution as the metal

source. They were applied to catalyze the hydrogenation of CO₂ to FA. The results showed that the catalytic hydrogenation performance could be significantly improved by the N doping modification.

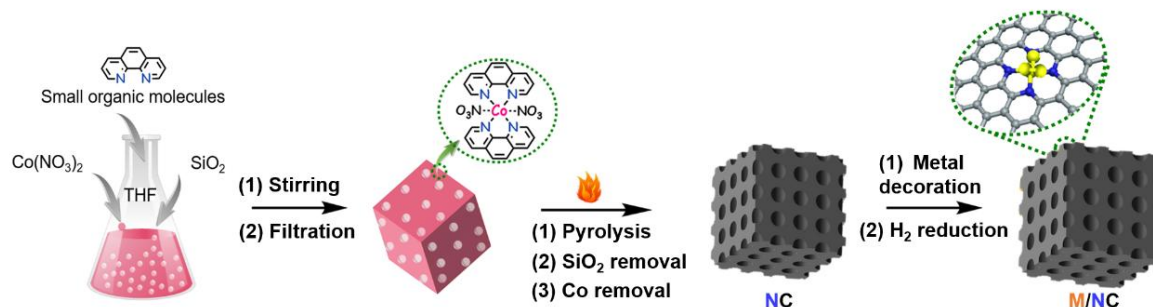


Fig. 1 Scheme of the synthesis of catalysts.

2. Experiment

2.1 Materials

1,10-phenanthroline (98%), 2,2-dithiophene (AR), SiO₂, THF, NaOH, H₂SO₄, Co(NO₃)₂·6H₂O, H₂IrCl₆·6H₂O, RuCl₃·3H₂O, RhCl₃·3H₂O, K₂PdCl₄, HAuCl₄, PtCl₂, AgNO₃ and In(NO₃)₃ were derived from Aladdin or Macklin and were used directly without further purification.

2.2 Characterization

The structure of the catalyst was characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM), raman spectral analysis (Raman), energy dispersive X-Ray spectroscopy (EDS), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS), nitrogen adsorption desorption analysis, etc.

The concentration of FA was quantitatively determined by high-performance liquid chromatography (HPLC), using 50 vol.% as the mobile phase. Based on the external standard method, the standard curve equation of FA ($R^2 = 0.9999$) was obtained by calibrating FA solution with different concentration (20 mM, 40 mM, 50 mM, 100 mM and 200 mM).

TON (turnover number) and TOF (turnover frequency) were used to evaluate the catalytic activity of catalysts, which could be calculated by the following formula (1) and (2):

$$TON = \frac{n_{\text{formic acid}}}{n_{\text{metal}}} \quad (1)$$

$$TOF = \frac{n_{\text{formic acid}}}{t \cdot n_{\text{metal}}} \quad (2)$$

In the above equation, TON, TOF, n, and t represent turnover number, turnover frequency, amount of substance, and time respectively.

2.3 Preparation of catalyst

(1) Synthesis of carbon material carrier. 1,10-phenanthroline (2 g), SiO₂ (2 g) and Co(NO₃)₂·6H₂O were added to 100 ml THF solution to form a mixed solution. And then, the mixture solution was stirred for 6 hours at 60 °C under nitrogen atmosphere. After that, the solid sample was obtained by rotating evaporation to remove the excess solvent in the mixed solution and continued to dry overnight in a vacuum oven at 60 °C. The black powder was obtained by calcinating the above solid sample at 800 °C for 2 h in nitrogen atmosphere. After the reaction, the black powder was washed successively with 1 M NaOH, 1 M H₂SO₄, and finally distilled water, and then dried to obtain N-doped carbon materials (NC). Similarly, S-doped carbon materials (SC) could be obtained by the same preparation process, which required only the replacement of 1,10-phenanthroline with equal mass of 2,2-dithiophene.

(2) Synthesis of M/NC and M/SC. The 100 mg carbon material carrier was suspended in 20 ml water and ultrasounded until evenly dispersed. A metal solution was then added to the above solution to form a mixed solution. And then, the mixed solution was ultrasonic for 1 hour, continued to stir at room temperature for 12 hours, and finally steamed to remove the solvent to get a dry powder. The M/NC and M/SC (M = Ir, Ru, Au, Ag, Rh, Pd, In, Pt) were obtained by calcinating the above dry powder at 250 °C for 2 h in 8% H₂/Ar atmosphere.

3. Results and discussions

3.1 Synthesis and structural analysis

As shown in Fig. 2a and 2b, the NC and SC carrier materials exhibited amorphous carbon morphologies with abundant mesoporous structures on the surfaces (the pore size was mainly distributed around 5-10 nm). Moreover, as shown in Fig. 2c, after the NC carrier material loaded with Ir metal, the specific surface area decreased slightly from 750.262 m²/g to 726.916 m²/g, indicating that the catalyst still had a mesoporous structure to ensure rapid mass transfer and efficient utilization of Ir site. HRTEM images (Fig. 2d and 2e) showed that Ir nanoparticles with small diameter (about 7-8 nm) and crystal face spacing ($d(111) = 2.0 \text{ \AA}$, $d(200) = 1.716 \text{ \AA}$) could be observed at higher magnification. From the PXRD images (Fig. 2f), it can be seen that all materials had obvious wide diffraction peaks at $2\theta = 24\text{-}26^\circ$, 43° , indicating that the precursor was completely carbonized as graphitic carbon and the Ir metal species were uniformly dispersed. As shown in the Raman spectroscopy (Fig. 2g), NC and SC materials were proved to have abundant defect sites, where the values of ID/IG were 1.021 and 1.033, respectively. As shown in the Fig. 2h and 2i, the peaks in the N 1s XPS spectrum of Ir/NC at about 397.7 eV, 400.1 eV, 401.3 eV and 399.8 eV were assigned to pyridine N, pyrrole N, graphite N, and coordination N species, respectively. Meanwhile, the peaks in the Ir 4f spectra (4f_{5/2} and 4f_{7/2}) were mainly divided into two types, which ascribed to the oxidation state Ir⁴⁺ (61.64 eV, 64.64 eV) and the metal state Ir⁰ (60.43 eV, 63.43eV). Moreover, the peak area of Ir⁴⁺ was much larger than that of Ir⁰, indicating that a trace amount of Ir existed in the form of nanoparticles.

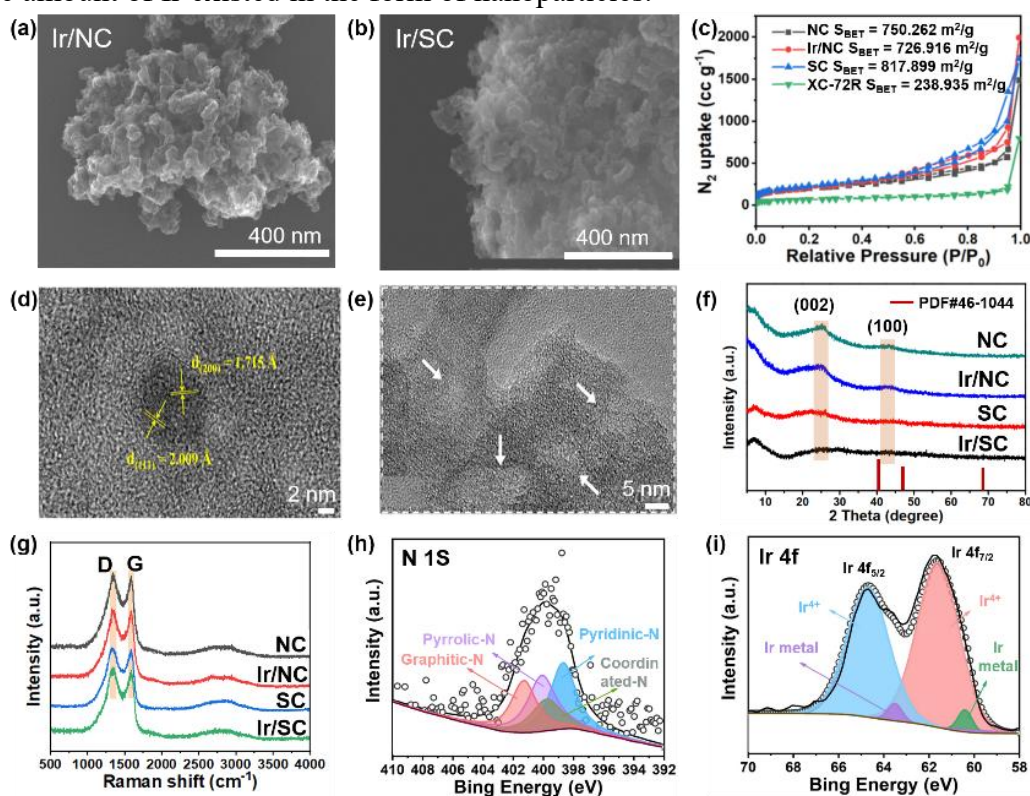


Fig. 2 SEM images of Ir/NC (a) and Ir/SC (b); (c) N₂ adsorption-desorption isotherms of NC, SC, XC-72R carbon materials and Ir/NC catalyst; (d) and (e) HRTEM images of Ir/NC catalyst; (f) XRD spectra of NC, Ir/NC, SC and Ir/SC; (g) Raman spectra of NC, Ir/NC, SC and Ir/SC; (h) N 1s and (i) Ir 4f XPS spectra of Ir/NC.

3.2 Catalytic performances of CO₂ hydrogenation to FA

Firstly, the catalytic activities of different metals and support materials were tested and compared (Fig. 3a insert). Compared with other metals, Ir exhibited the unique activity for hydrogenation of CO₂ to FA. In addition, the catalytic performance of Ir on different support materials was also different (Fig. 3a), with the order of Ir/NC>Ir/SC>Ir/XC-72R, indicating that the doping of N element played a significant role in enhancing the catalytic activity [9]. The TON of Ir/NC for FA could reach 987 at 120 °C, 8 h and 6 MPa (CO₂:H₂ = 1:1, v/v). As shown in Fig. 3b, the catalytic activity of Ir/NC gradually decreased with the increase of metal loading due to the size of Ir nanoparticles gradually increased, thus leading to a decrease in the number of surface atoms and surface/boundary atoms with higher activity. As shown in Fig. 3c, the catalytic activity of the Ir/NC substantially increased when the reaction temperature increased from 120 to 150 °C, and showed the optimal activity at 150 °C. Moreover, the activation energy of CO₂ hydrogenation to FA on Ir/NC was calculated to be $E_a = 52.606$ J/mol [10]. The dependence of catalytic activity on pressure (Fig. 3d) was studied at a constant pressure ratio (CO₂:H₂ = 1:1, V/V) between 3 MPa and 6 MPa, which showed that with the increase of total pressure, catalytic activity significantly increased with a change in TON from 346 to 987. In addition, as shown in Fig. 3e, when the reaction time was extended to 48 h, TON increased significantly and reached 3901, indicating that Ir/NC had considerable stability and could maintain the high catalytic activity for a long time. Moreover, it can also be observed from the cycling test (Fig. 3f) that the catalyst can be reused 4 times with no obvious loss of activity, indicating the good stability of the obtained catalyst.

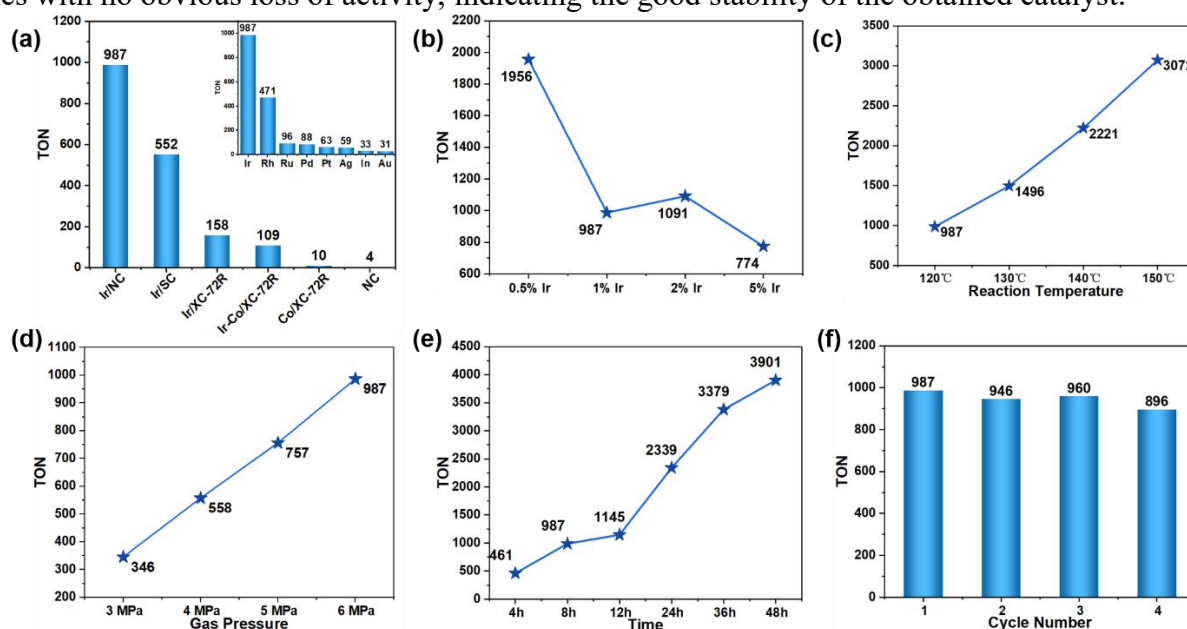


Fig. 3 (a) Comparison of the performances for different catalysts; (b) Comparison of the effects of supporting metal contents of Ir/NC catalyst; (c) Influences of temperature; (d) The effect of reaction pressure; (e) Time courses of CO₂ hydrogenation to FA with Ir/NC catalyst; (f) Recyclability of Ir/NC catalyst. General reaction condition: 5 mg catalyst powder, 10 mL 1 M KHCO₃, P(H₂)/P(CO₂) = 3/3 MPa, 120 °C, 8 h.

3.3 Catalytic mechanism for CO₂ hydrogenation to FA

A possible mechanism for CO₂ hydrogenation was presented on the Ir/NC combined with previous studies[11]. N exhibited more electronegative properties than S and C to attract

surrounding electrons, resulting in the formation of a strong localized electron cloud around the N site. Therefore, Ir could be stably anchored to NC, and at the same time the appropriate electron transfer occurred between NC and Ir, thus forming the oxidation state Ir δ^+ . First, the reaction was initiated by the dissociation of H₂ to afford a Ir-H species. Synchronously, HCO₃⁻ was formed by the conversion of CO₂ in an alkaline solution and adsorbed on Ir δ^+ . After that, HCO₃⁻ reacted with H to remove an O atom in the form of H₂O, creating the intermediate HCOO⁻. Based on the metal-carrier interaction, the efficiency of H₂ splitting and the conversion of HCO₃⁻ to HCOO⁻ were both improved.

4. Summary

In this work, the catalyst Ir/NC was successfully designed and synthesized by loading Ir nanoparticles on N-doped carbon carrier material, and was further applied to catalyze the hydrogenation of CO₂ to FA. The results showed that the N doped Ir/NC catalyst had a better catalytic performance than S doped Ir/SC catalyst. In summary, the element-doped carbon-based catalyst with a well-defined active center could be constructed by calcining the metal-small molecule complex strategy and reducing the supported metal with hydrogen at a low temperature. Moreover, the catalytic performance was obviously related to the type and proportion of doped elements, which provided a detailed guidance for the design of highly efficient heterogeneous catalysts for CO₂ hydrogenation to FA.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51972342), Taishan Scholar Project of Shandong Province (No. ts20190922), Key Basic Research Project of Natural Science Foundation of Shandong Province (No. ZR2019ZD51).

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