Zeolitic imidazolate frameworks derived nitrogen doped porous carbon for electrochemical reduction of CO₂

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Abstract. The development of high-performance electrochemical materials plays an important role in CO₂ reduction efficiency and cost effectiveness. In this work, nitrogen doped porous carbon matrix was designed and fabricated from zeolitic imidazolate frameworks (ZIF-8). Pyrolysis temperature was investigated to achieve the best performance to convert CO₂ into CO. The suitable temperature is 700 °C which could make the catalyst containing good conductivity and activity. The highest Faradaic efficiency of CO is close to 25% at potential of -1.0 V.

1. Introduction
Carbon dioxide (CO₂) is a major source of greenhouse gas in atmosphere, which is thought to cause severe environmental issues such as global warming [1]. From another point of view, however, CO₂ is a cheap and non-toxic carbon resource. Hence, conversion of CO₂ into fuels and high-valued chemicals is a suitable way to alleviate the pressure of environmental crisis of greenhouse gas emission and conventional fossil fuels [2, 3].

Electrochemical reduction supported by sustainable electric energy is one of the most promising approaches to achieve green conversion of CO₂, which has attracted enough attention from many researchers in the past decades [4]. Because CO₂ is a chemically stable and inert molecule, developing highly efficient and stable electrocatalyst for activating CO₂ is the key problem in this hot field.

In recent years, precious metals, such as Au, Ag, Pd based materials, have been widely studied to electrocatalytic reduction of CO₂ into formate and CO [5-11]. Although some of precious metals made good performance, their rare reserves and high cost greatly hinder their commercialization progress. Therefore, the development of non-precious metal catalyst for this reaction become very necessary and urgent.

Heteroatom doped porous carbon material (HPC) is a kind of effective electrocatalysts with high porosity, good electric conductivity, hetero atom doping and easy to prepare, which has been widely studied for oxygen reduction reaction (ORR) and water splitting reaction [12-14]. For electrochemical CO₂ reduction, a variety of HPC have been reported and obtain excellent achievement [15, 16]. Recently,
zeolitic imdazolate frameworks (ZIFs) is a novel class of high specific surface, high porosity and high N content carbon material, which is widely used as sacrificial template to prepare N doped porous carbon-based materials [17].

In this work, Zn-based ZIF-8 is used as the precursor to synthesize N doped porous carbon matrix (NPC), the as-prepared NPC exhibits catalytic activity for CO$_2$ reduction to produce value-added carbon monoxide (CO).

2. Experiment

Chemicals: 2-methylimidaze, Zn(NO)$_2$·6H$_2$O, methanol, KHCO$_3$, were purchased from Sigma-Aldrich, Nafion solution (15 wt% in ethanol) was purchased from Ion Power. Deionized water used in this work was obtained via Millipore system.

Preparation of ZIF-8: 3.36g Zn(NO)$_2$·6H$_2$O was first dissolved in 60 mL methanol, which was named as solution A, 8 g 2-methylimidaze was dissolved in 100 mL methanol, which was named as solution B. Then solution A and B were mixed and sitred for 1 h, and then kept it without stir for 24 h. After that, white precipitate was collected and wash with methanol for several times and dried at 70 °C overnight.

Preparation of NPC: The as-prepared ZIF-8 was pyrolyzed at a desirable temperature for 2 h with a ramp rate of 5 °C min-1 in Ar atmosphere, then cooled to room temperature naturally.

Materials Characterization: X-ray diffraction (XRD, MiniFlex 600, Rigaku) was carried out to analyze crystallite structure. Transmission electron microscopy (JEOL 2010F) was used to characterize the morphology of as-prepared catalyst.

Electrochemical Measurement: The catalyst ink was first prepared by mixing 2 mg as-prepared catalyst and 160 µL ethanol and 32 µL of 5 wt% Nafion ethanol. Then the ink was sonicated for 1 h and dropped it onto a carbon paper (1 cm$^2$) with gas diffusion layer (GDL). The electrochemical CO$_2$ reduction measurement was carried out in a gas tight H-type cell. The electrolyte was 0.5M KHCO$_3$.

Products Analysis: Gas phase samples were analyzed by GC-HID (gas chromatography with helium ionization detector)

3. Results and discussion

3.1. ZIF-8 derived NPC catalyst characterization

ZIF-8 was first prepared at room temperature and then pyrolyzed at 500 °C, 700 °C and 900 °C which are named as NPC-500, NPC-600 and NPC-900. TEM images show that the fresh ZIF-8 with well-formed rhombic dodecahedral structure and uniform size around 100-150 nm (Figure 1a). After treated with pyrolysis process, the dodecahedral structure of ZIF-8 destroyed obviously, higher temperature lead to the higher degree of collapse, which is confirmed by TEM images (Figure 1b-d). Photographs of as-prepared catalysts show that white ZIF-8 was convert to khaki color powder at 500 °C, while black powder can be obtained at higher pyrolysis temperature, such as 700 °C and 900 °C (Figure 1e). XRD patterns (Figure 1f) show that diffraction peaks of NPC-500 is the same as the ZIF-8, indicating that part of crystal structure maintained after treated at 500 °C. For NPC-700 and NPC-900, no obvious peaks are observed, suggesting that ZIF-8 is complete converted into porous carbon matrix.
3.2. Electrochemical reduction of CO$_2$

Linear sweep voltammetry (LSV) technique was first conducted to investigate catalytic activity of NPC-500, NPC-700 and NPC-900 in the CO$_2$ saturated KHCO$_3$. As shown in Figure 2a, NPC-500 shows the lowest current density. Because the crystal structure of ZIF-8 maintains in NPC-500, pyrolysis temperature of 500 °C is too low to obtain a good electric conductivity of NPC-500, which result in low current density. NPC-700 and NPC-900 exhibit higher current density which ascribes the higher temperature such as 700 °C and 900 °C could generate high graphitization carbon material possessing excellent electric conductivity. Figure 2b shows the Faradaic efficiency (FE) of CO for NPC-500, NPC-700 and NPC-900. NPC-700 exhibits the best performance for CO production, the highest FE of CO is close to 25% at the potential of -0.9 V and -1.0 V. As counterparts, NPC-500 can obtain 21.9% of CO FE at -1.1 V, however, the potential is higher than that of NPC-700, which increase the energy consumption. The performance of NPC-900 is very poor, the CO FE cannot reach 15% in the potential range from -0.8 V to -1.1 V, even the current density is the highest. The good performance of NPC-700 may be attribute to the suitable conductivity and active sites. While lower temperature such as 500 °C
cannot provide good conductivity, and the higher temperature such as 900 °C could result in the loss of active sites.

Figure 2. (a) LSV curves of NPC-500, NPC-700, NPC-900 in CO$_2$-saturated 0.5 M KHCO$_3$, (b) FE of CO with NPC-500, NPC-700, NPC-900 as catalysts.

4. Conclusion

NPC materials were synthesized via a simple pyrolysis process from porous ZIF-8. The performances of CO$_2$ reduction show that 700 °C is a suitable pyrolysis temperature for obtaining the good conductivity and active NPC. The highest CO FE is close to 25% at the potential of -1.0 V. These results give a good way to build NPC for catalytic conversion of CO$_2$.

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