



Sulfur and nitrogen co-doped mesoporous carbon with enhanced performance for acetylene hydrochlorination

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ABSTRACT

Acetylene hydrochlorination is a major technology for producing vinyl chloride in coal-rich areas, but its development is restricted by its utilizing the toxic mercury chloride (HgCl_2) catalyst. Lately, several nitrogen-doped carbon materials have been studied and are considered to be a feasible alternative. Here, we propose an approach based on sulfur doping to effectively improve the pyridinic N content in N-doped carbon material. According to high-resolution XPS and C_2H_2 TPD results, C atoms adjacent to pyridinic N were proved to be active sites, and thus the co-doped carbon catalyst exhibited a higher acetylene conversion than the N-doped carbon sample. Furthermore, the co-doped catalyst processed in NH_3 exhibits preferable catalytic activity and competitive stability owing to its high specific surface area, mesoporous structure, and high nitrogen level. Good performance, combined with the features of low cost and ecofriendliness, makes sulfur and nitrogen co-doped carbon a promising catalyst for acetylene hydrochlorination.

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1. Introduction

Polyvinyl chloride (PVC) is one of the most widely used general-purpose plastics around the world. Because of China's "deficient oil, lean gas, rich coal" energy structure, vinyl chloride monomer (VCM), the major chemical intermediate for manufacturing PVC, is primarily produced by hydrochlorination of acetylene in China, with mercuric chloride (HgCl_2) supported on activated carbon (AC) as the catalyst [1,2]. Nevertheless, toxic and volatile HgCl_2 is liable to be lost during the reaction and will do great harm to the environment and the health of humanity. Owing to the negative effects of HgCl_2 catalyst, the United Nations had planned to prohibit its use worldwide in the near future. Moreover, more than 140 countries signed the Minamata convention on mercury in 2013 and promised to reduce and eventually eliminate the use of mercury by 2020 [3]. Therefore, in order to guarantee the sustainable production of PVC, it is urgent to develop environmentally friendly nonmercury catalysts for acetylene hydrochlorination [4].

Replacing HgCl_2 with other metal chlorides is a feasible approach, and many catalysts, such as Cu [5], Pd [6,7], Pt [8,9], Bi

[10], and Ru [11,12] chlorides, have been investigated. Based on numerous and systematic studies, Hutchings and co-workers proposed that Au catalysts with considerable acetylene conversion and impressive stability are the best alternative to HgCl_2 for acetylene hydrochlorination [13–15]. In addition, they developed bimetallic gold and gold complex catalysts to decrease the Au loading further and improve the catalyst stability for meeting the requirements of industrial production [1]. However, scarce resources and high cost greatly restrict the sustainable utilization of Au catalysts, which prompts scientists to explore other strategies for acetylene hydrochlorination catalysts.

In the last few years, nitrogen-doped carbon materials have gained a great deal of attention due to their unique properties and have been found quite useful in extensive applications [16]. Researchers found that they also show acceptable catalytic activity in acetylene hydrochlorination. Bao and co-workers reported that N-doped carbon derived from silicon carbide manifested high and stable acetylene conversion during a 150 h test, and they considered that carbon atoms bonded with pyrrolic N atoms are active sites [17]. Wei et al. also found that nitrogen-doped carbon nanotubes were active for this reaction, and revealed good linearity between the quaternary nitrogen content and acetylene conversion [18]. Dai's group introduced several nitrogen-containing catalysts supported on AC using cyanamide, melamine, or aniline as doping precursors, and these materials all exhibited improved

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catalytic activity compared with undoped AC [19–21]. They believed that pyrrolic N played the most important role in the reaction. More recently, our group developed a N-doped porous carbon derived from ZIF-8 (a metal–organic framework material) with fairly good activity and stability for acetylene hydrochlorination, and both experimental and theoretical studies indicated that C atoms adjacent to the pyridinic N atoms are the active sites [22]. Overall, in consideration of the low cost and environmental acceptability, N-doped carbon materials stand a good chance of becoming a promising catalyst for the sustainable production of vinyl chloride. However, to meet the requirements of practical use, it is still a challenge to further improve the catalytic activity of N-doped carbon catalysts by appropriate modifications. Beyond that, the nature of the active sites of the catalyst also needs to be elucidated to uncover the effect of N species.

Recently, a dual doping strategy was utilized to improve the tuning of N-doped carbon catalytic activity [23]. The obtained catalyst with incorporated boron and nitrogen possessed higher acetylene conversion than the N-doped sample, even though its stability was poor. This finding inspires us to research multiple doping of carbon materials for acetylene hydrochlorination. As a nonmetallic element, sulfur often has a synergistic effect with nitrogen in carbon materials, resulting in performance improvement for some applications [24,25]. Meanwhile, it is reported that the use of mesoporous carbon in acetylene hydrochlorination enables fast molecular diffusion and thus reduce the impact of coke [26]. Therefore, we utilize a sulfur and nitrogen co-doping strategy to fabricate a mesoporous carbon catalyst for acetylene hydrochlorination, finding that it can improve the pyridinic N content effectively and thus shows enhanced acetylene conversion compared with the N-doped carbon catalyst. Based on the evaluation result and various characterizations, C atoms adjacent to pyridinic N are proved to be the active sites of the doped carbon catalyst for the reaction. Furthermore, the high specific surface area together with the mesoporous structure derived from SBA-15 and high nitrogen level ascribed to the NH_3 treatment result in excellent catalytic stability of the co-doped catalyst, allowing its practical application.

2. Experimental

2.1. Materials

Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), thiourea (H_2NCSNH_2 , 99%), urea (H_2NCONH_2 , 99%), hydrofluoric acid (HF, 40%), and ethanol ($\text{C}_2\text{H}_6\text{O}$) were purchased from Tianjin Guangfu Technology Development Co., Ltd. Benzyl disulfide (BDS, 98%) was obtained from Aladdin Industrial Corporation. Mesoporous SBA-15 was purchased from Nanjing XFNANO Materials Tech Co., Ltd. All of the materials were analytical grade and utilized without further purification. Deionized water used in the experiments was supplied by an Ulupure system ($18.25 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Preparation of doped mesoporous carbon

In a typical process, sucrose (0.8 g) and thiourea (1.6 g) were dissolved in deionized water (5 mL) with stirring and appropriate heating to prepare an impregnated solution. Subsequently, the solution was added dropwise to 1 g mesoporous SBA-15 silica under stirring, followed by incubation for 12 h at room temperature. After drying at 60°C for 24 h, the mixture was calcined at 300°C for 1 h and then carbonized at 650°C for 4 h at the same heating rate of 5°C min^{-1} under flowing N_2 . When cooling to room temperature, the obtained sample was plunged into HF solution to remove the silica template. Finally, a black powder, denoted as

NS-C-N_2 , was separated by air pump filtration, washed several times with deionized water and ethanol, and dried in air at 120°C . For comparison, another three samples were prepared by the same procedure. Pure carbon (C-N_2) was fabricated without adding thiourea. N-doped carbon (N-C-N_2) was synthesized using urea as a dopant because of the similar molecular structure of thiourea and urea. NS-C-NH_3 refers to sulfur and nitrogen co-doped carbon heated under NH_3 rather than N_2 .

Sulfur-doped carbon (S-C-N_2) was fabricated using the same method, with BDS as the dopant. First, 1 g of SBA-15 silica was impregnated with an aqueous solution (5 mL) containing 0.8 g of sucrose. After drying at 60°C for 24 h, the mixture was dispersed in ethanol solution (20 mL) containing 2.6 g of BDS. After 4 h of stirring, the ethanol in the solution was volatilized gradually at 50°C , and as a result a solid powder was obtained. Then the powder was calcined, plunged into HF solution, washed, and dried as in the procedure mentioned above to gain a carbon sample doped by sulfur.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 focus diffractometer using $\text{Cu K}\alpha$ radiation to characterize the crystalline structure. The size and morphology of as-obtained samples were observed by field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL) and transmission electron microscopy (TEM, G2 F20, FEI Tecnai) with a linked energy-dispersive X-ray (EDX, TEAM, EDAX) system for elemental mapping. Nitrogen adsorption/desorption isotherms were obtained at 77 K on a BELSORP-Max instrument with the samples preprocessed in vacuum at 300°C for 12 h. The specific surface area data and the pore size distribution analysis were calculated by Brunauer–Emmett–Teller (BET) and nonlocal density functional theory (NLDFT) methods, respectively, from the adsorption isotherm. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD spectrometer using 250 W Al $\text{K}\alpha$ radiation with the $\text{C}1\text{s}$ peak at 284.6 eV as the internal standard. Temperature-programmed desorption (TPD) for C_2H_2 was performed on a Micromeritics Chemisorb 2750 instrument over the temperature range $50\text{--}600^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$ and a He flow rate of 25 mL min^{-1} . Thermogravimetric (TG) analysis was conducted using a thermogravimetric analyzer (TG-DTA, S60, SETARAM). Elemental analysis was performed with an elemental analyzer (EA, Vario EL CUBE, Elementar).

2.4. Catalytic activity evaluation

The catalytic performance of the catalysts was evaluated using a fixed-bed microreactor (i.d. 10 mm); 0.25 g of sample was added to the reactor for each test. Due to different bulk densities, the volumes of carbon catalysts are diverse. To make the contact time as consistent as possible, silica sand was mixed with the catalyst to expand the volume to 3 mL. In a typical process, nitrogen was employed first to remove the moisture and air in the reaction system. Then hydrogen chloride (HCl) gas was introduced into the reactor with a flow rate of 5 mL min^{-1} for 1 h at 220°C to activate the catalyst. After activation, reaction gases, HCl (1.6 mL min^{-1}) and acetylene (1.3 mL min^{-1}), with a volume ratio of 1.2, were fed through the heated reactor, giving rise to a gas pressure of 1 kPa. The gas effluent was passed through an absorption bottle containing clean water and then analyzed by an online gas chromatograph. The acetylene conversion (δ) was calculated as follows:

$$\delta = M_{\text{vc}} / (M_{\text{vc}} + M_{\text{r}}) \times 100\%.$$

Here, M_{vc} represents the moles of vinyl chloride and M_{r} the moles of the remaining acetylene in the mixture.

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