



Effect of carbon defects on the nitrogen-doped carbon catalytic performance for acetylene hydrochlorination

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ABSTRACT

The carbon defects in nitrogen-doped carbon were controlled by removing the N atoms under different temperatures during the catalyst preparation process. The synthesised catalysts were characterised by multiple techniques, and the catalytic performance was evaluated under experimental conditions of gas hourly space velocity (C_2H_2) = 36 h^{-1} at $220\text{ }^\circ\text{C}$. The catalytic performance of the synthesised nitrogen-doped carbon for acetylene hydrochlorination increased with the increment of carbon defect. Carbon defects in the catalysts were proposed to affect the adsorption of C_2H_2 and HCl and promote their conversion. The regeneration of the nitrogen-doped carbon catalyst was found to be effective by using high-temperature treatment in an NH_3 atmosphere.

1. Introduction

Acetylene hydrochlorination is a very important method for manufacturing vinyl chloride monomer (VCM) in China because China contains rich deposits of coal but lacks oil. However, the industrial catalyst for acetylene hydrochlorination is $HgCl_2$, which is toxic to the human body and the environment [1]. Therefore, the exploitation of environmentally friendly non-mercury catalysts is attracting increasing attention for acetylene hydrochlorination.

In the past decades, Au catalysts have been found to be effective for acetylene hydrochlorination. In our previous work, we designed an Au catalyst whose acetylene conversion rate reached 100%. This catalyst could be stably used for 6513 h under industrial application conditions [2,3]. Wei et al. [4] found that a Au catalyst with thiocyanate ligands could operate for over 3000 h in a 4 t per annum scale pilot experiment. Hutchings et al. [5] reported very exciting results for the development of non-mercury acetylene hydrochlorination catalysts. By using thio ligands as soft donor atoms, active Au^+ and Au^0 were present consistent with the formation and deposition of Au catalyst, and the synthesised catalyst could last over 3000 kg VCM/kg catalyst, which is a very low Au loading. These investigations greatly accelerated the commercialisation of non-mercury catalysts for acetylene hydrochlorination. However, given the high cost and scarcity of Au, low-cost catalysts are being sought as non-mercury replacement catalysts for acetylene hydrochlorination.

In our previous work, we synthesised C_3N_4 for acetylene hydrochlorination, and we found that the acetylene conversion rate of this catalyst can reach 75% of the $HgCl_2$ catalyst efficiency. According to density functional theory (DFT) calculations, carbon atoms were the adsorption sites for acetylene, and nitrogen atoms were the adsorption sites for hydrogen chloride [6]. The reaction activation energy was 77.94 kcal/mol , which is much higher than $AuCl_3$ (11.9 kcal/mol) [7]. Thereafter, many groups have synthesised catalysts with nitrogen-doped carbons that display excellent catalytic performance. Wei et al [8]. reported nitrogen-doped carbon nanotubes that could greatly enhance the adsorption of acetylene. This catalyst showed excellent catalytic properties with turn over frequency (TOF) of up to $2.3 \times 10^{-3}/s$. Pan et al. [9] found that the catalyst activity increased with increasing N content, and only carbon atoms linked to pyrrolic nitrogen could adsorb acetylene. Thus, they found that the type of nitrogen played a major role in this reaction. The catalyst performance stabilised at above 80% under 30/h (C_2H_2) and $200\text{ }^\circ\text{C}$ during 150 h. In our previous work, we considered the effect of the nitrogen species in the nitrogen-doped catalyst for acetylene hydrochlorination and found that the effectiveness of the nitrogen species for acetylene hydrochlorination followed this order: pyrrolic N > graphitic N > pyridinic N [10]. On the basis of that sequence, we then designed and synthesised boron and nitrogen dual-doped graphene (B, N-G) materials. The acetylene conversion on that catalyst could reach to 95%, which was very close to the performance of Au and Hg catalysts [11].

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Although obvious progress has been made in carbon-based catalysts for acetylene conversion, it must be noted that the TOF on a single active site of the carbon-based catalyst is still much lower than that of an Au or Hg catalyst [11], and the stability of the carbon-based catalyst still needs improvement. In designing and synthesising carbon-based catalyst with better activity and stability, it is important to find the relationship between the physical properties and catalytic performance. Carbon defects in nitrogen-doped carbon can significantly affect the catalytic activity of the oxygen reduction reaction [12–14]. Therefore, we were extremely curious if carbon defects in our carbon-based catalyst may also affect the catalytic performance for acetylene hydrochlorination. Therefore, we investigated the adsorption ability of C₂H₂ and HCl on mono-vacancy graphene, di-vacancy graphene and stone-wales defect graphene by using DFT calculations. We found that carbon defects could enhance the adsorption capacity for C₂H₂ and HCl [15]. In this work, we controlled the synthesis of carbon defects during nitrogen-doped carbon synthesis by removing N atoms under high temperature and characterised the carbon defects by using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The catalytic performance was evaluated using a fixed-bed reactor. Temperature-programmed decomposition (TPD) experiments were used to characterise the reactant adsorption on the surface of the catalyst. Furthermore, the influence of defect on the N-doped carbon was elucidated by DFT calculations.

2. Experimental

2.1. Catalyst preparation

All materials, unless otherwise specified, were obtained from Aldrich Chemical Co. C₂H₂ (acetylene gas, 99%) and HCl (hydrogen chloride gas, 99%) were used in this study. The catalysts were synthesised by following the procedure reported in Refs [16,17]. (i) 2,4,6-Tris(p-nitroanilino)-1,3,5-triazine was obtained as follows: cyanuric chloride (2.31 g), p-nitroaniline (8.65 g) and K₂CO₃ (10.4 g) were added into 1,4-dioxane (120 ml). After refluxing for 24 h, the products were sequentially washed with deionised water, methanol and benzene and then filtered and dried under vacuum overnight. (ii) 2,4,6-Tris(p-aminoanilino)-1,3,5-triazine was then synthesised. SnCl₂·2H₂O (~20.7 g) was dissolved in HCl solution (12 M, 30 ml). The obtained 2,4,6-tris(p-nitroanilino)-1,3,5-triazine (4.89 g in 20 ml ethanol) was added in the above solution slowly and then refluxed for 48 h. After filtration, the resulting solid was re-dissolved in hot water; the pH was adjusted to 12 by using NaOH solution; and the precipitated product was sequentially washed with deionised water and methanol, filtered and then dried under vacuum overnight. (iii) Terephthaldehyde (50 mg), 2,4,6-tris(p-aminoanilino)-1,3,5-triazine (100 mg), anhydrous dioxane (5 ml) and aqueous acetic acid (3 M, 2 ml) were added to a Teflon-lined stainless steel autoclave. This was placed in an oven and kept at 120 °C for 7 d. The obtained powder was Soxhlet extracted in anhydrous THF for 72 h, dried at room temperature for 12 h and then dried at 70 °C for 2 h. A yellow powder was obtained after this sequence. (iv) The pyrolysis step was conducted at 700 °C, 900 °C and 1100 °C in N₂ atmosphere for 5 h at a ramp rate of 2 °C/min. Thereafter, the sample was degassed for 24 h at 180 °C. The catalysts were labelled C700, C900 and C1100.

2.2. Catalyst characterisation

XRD data were collected using a Bruker advanced D8 X-ray diffractometer using Cu-Kα irradiation (λ = 1.5406 Å) at 40 kV and 40 mA in the 2θ scanning range of 10° to 90°. Raman spectra were collected using a Horiba Jobin Yvon LabRAM HR800 (633 nm laser excitation). Thermogravimetric analysis was conducted using a TGDSC simultaneous thermal analyser (Netzsch Sta 449F3 Jupiter1, Germany). XPS data were collected using a Thermo ESCALAB 250XI with Al, Ka X-ray source (225 W). TPD was recorded with an AutoChem 2720

instrument (Micromeritics Instrument Corporation, USA), and the ramp rate was 10 °C/min, the flow rate was 40 ml/min under Ar atmosphere. The experiments were carried out over a temperature ramp of 25 – 600 °C, ramp rate of 10 °C/min, and flow rate of 40 ml/min under nitrogen atmosphere.

2.3. Description of catalytic tests and analytical criteria

The catalyst performance was evaluated using a fixed-bed micro-reactor (inner diameter: 10 mm). A CKW-1100 temperature controller was used to control the temperature. The air in the microreactor with catalyst (0.5 g, 2 ml) was replaced with nitrogen prior to commencing the reaction. Acetylene gas (1.2 ml/min) and hydrogen chloride (1.3 ml/min) were pumped into the reactor at a gas hourly space velocity (GHSV, C₂H₂) of 36/h, and the reaction temperature was 220 °C. A GC2014C with a FID (flame ionization detector) detector was used to analyse the reaction products. The conversion of acetylene (XA) and the selectivity of the catalyst to VCM (SVC) were calculated as follows:

$$X_A = (\Phi_{A0} - \Phi_A) / \Phi_{A0} \times 100\%,$$

$$S_{VC} = \Phi_{VC} / (\Phi_{A0} - \Phi_A) \times 100\%,$$

Where Φ_{A0} is the volume fraction of acetylene in the raw gas, Φ_A is the volume fraction of remaining acetylene in the product gas and Φ_{VC} is the volume fraction of vinyl chloride in product gas. The catalytic performance was further evaluated by TOF, which was calculated using the following equation.¹¹

$$\text{TOF} = \frac{n_{C_2H_2}}{n_N \cdot t}$$

Where n_N is the amount of substance of nitrogen atom in the catalyst, t is the reaction time, and $n_{C_2H_2}$ is the amount of substance of C₂H₂ in the time.

The adsorption behaviours was calculated by density functional theory (DFT) on catalyst. Gaussian09 software package was used to perform simulations [18]. The method is hybrid density functional method M062X [19]. In order to obtain more accurately results, a van der Waals energy correction has been applied by using the parameters defined by Grimme et al [20]. The cc-pVDZ basis set was applied for all atoms [21,22]. This basis set has been previously applied to produce reliable results in similar system [23]. The adsorption energy of HCl and C₂H₂ adsorbed on catalyst was calculated as :

$$E = E_{\text{system}} - E_{\text{adsorbates}} - E_{\text{catalyst}}$$

E is the adsorption energy; E_{system} is the total energy of adsorption complex; $E_{\text{adsorbates}}$ the total energy of isolated adsorbates; E_{catalyst} is the energy of isolated catalyst.

3. Results and discussion

Fig. 1 shows the XRD patterns of the C700, C900 and C1100 catalysts. Two obvious distinct diffraction planes were found at 23° and 43°, corresponding to the (0 0 2) and (1 0 1) diffraction planes of graphitic carbon [24]. The XRD patterns reveal no other impurities, thus indicating that the nitrogen-doped carbon materials were synthesised and the predecessor materials were carbonised. Nitrogen adsorption/desorption isotherms was used to analyze the physical structures of catalysts. The results of the total pore volumes and specific areas were listed in Table 1. The result shows that all catalysts were mesoporous material.

During carbonisation, the loss of nitrogen atoms could form single-atom vacancies. Owing to the instability of a single-atom vacancy, two vacancies will combine to form divacancies. Divacancies include one octagon and two pentagons, which is usually treated as a G585 carbon defect (a topological defect which was combined by two pentagons and one octagon). If the loss of the nitrogen atom becomes greater, more carbon defects are produced [16,25–27]. Table 2 lists the elemental

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