



Catalysis, Kinetics and Reaction Engineering

Oxygen and nitrogen-doped metal-free carbon catalysts for hydrochlorination of acetylene[☆]

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ABSTRACT

Activated carbon was tested as metal-free catalyst for hydrochlorination of acetylene in order to circumvent the problem of environment pollution caused by mercury and high cost by noble metals. Oxygen-doped and nitrogen-doped activated carbons were prepared and characterized by XPS, TPD and N₂ physisorption methods. The influences of the surface functional groups on the catalytic performance were discussed base on these results. Among all the samples tested, a nitrogen-doped sample, AC-n-U500, exhibited the best performance, the acetylene conversion being 92% and vinyl chloride selectivity above 99% at 240 °C and C₂H₂ hourly space velocity 30 h⁻¹. Moreover, the AC-n-U500 catalyst exhibited a stable performance during a 200 h test with a conversion of acetylene higher than 76% at 210 °C at a C₂H₂ hourly space velocity 50 h⁻¹. In contrary, oxygen-doped catalyst had lower catalytic activities. A linear relationship between the amount of pyrrolic-N and quaternary-N species and the catalytic activity was observed, indicating that these nitrogen-doped species might be the active sites and the key in tuning the catalytic performance. It is also found that the introduction of nitrogen species into the sample could significantly increase the adsorption amount of acetylene. The deactivation of nitrogen-doped activated carbon might be caused by the decrease of the accessibility to or the total amount of active sites. © 2015 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

The production of vinyl chloride directly from acetylene via hydrochlorination has attracted great interests in China due to the rich coal reserves. However this progress is restricted by the volatility and toxicity of the mercury chloride catalyst adopted. Therefore, alternative catalysts with various metals have been investigated [1–8]. Among these metal catalysts, AuCl₃ is proved to be highly active and selective to the desired products. But the commercialization of this catalyst is largely hindered by the high cost and low catalytic stability since AuCl₃ is readily reduced to Au⁰ under reaction conditions [2,4,9–19]. The replacement of AuCl₃ with a less expensive metal, or even a metal-free catalyst having a higher stability, is required for practical purposes [20–25].

Nitrogen-doped carbon and carbon nitride materials are known to act as promising metal-free catalysts for several reactions because the incorporation of nitrogen atoms in the carbon architecture provides the access to an even wider range of applications than pure carbon materials [26]. Recently, some research efforts have been increasingly focused on the use of N-doped carbon materials as catalyst materials for the reaction of acetylene hydrochlorination. Dai *et al.* reported that a supported g-C₃N₄

catalyst on activated carbon (AC) was active for the gas phase hydrochlorination of acetylene [21]. Wei *et al.* evaluated the catalytic activity and stability of nitrogen-doped carbon nanotubes (N-CNTs) catalysts and found that N-CNTs were active for acetylene hydrochlorination reaction, possessing a good activity (TOF = 2.3 × 10⁻³ · s⁻¹) and high selectivity (>98%) [23]. Very recently, Bao *et al.* reported that a nanocomposite of nitrogen-doped carbon derived from silicon carbide could also activate acetylene directly for hydrochlorination [25]. By employing the pyrrolic materials, the acetylene conversion was twice that of SiC@N-C under the same conditions, but they were less suitable for industrial practice because of their powder nature.

To evaluate the potential of nitrogen-doped carbon materials as metal-free catalysts, it is desirable and interesting to first examine the influence of surface functional groups of carbon materials on the catalytic behaviors. As we all know, the nature of surface functional groups of the support is extremely important because they can dramatically affect the catalytic performance of the carbon-based catalysts by varying their acid-base and/or hydrophilic characters on carbon surface [27, 28]. For instance, it has been shown that carbonyl/quinone groups were the active sites for the oxidative dehydrogenation of ethylbenzene to styrene, and a linear correlation between the activity of carbon catalysts and the concentration of active sites was established [29]. Interestingly, it has been pointed out that the catalytic performance and even the reaction mechanism for the carbonaceous catalyst could be completely different, depending on different amounts and types of surface oxygenated groups [30,31]. In the present work, the surface of a

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pristine AC material was modified by nitrogen doping and wet treatments with HNO_3 and the catalytic performance of these modified carbon materials was tested as catalysts for gas phase hydrochlorination of acetylene. The influence of the surface modifications on the reaction rate and the product selectivity was examined.

2. Experimental

2.1. Catalyst preparation

A commercial activated carbon NORIT ROX 0.8 (pellets of 0.8 mm diameter and 5 mm length) was selected as the starting materials for the preparation of catalysts. The activated carbon was first pretreated with HNO_3 (65 wt%) (room temperature for 12 h) to introduce surface oxygenated groups. The pretreated activated carbon was then filtered, rinsed by deionized water until neutral and eventually dried at 110 °C for 12 h (AC-n).

The AC-n sample was used as the starting material for thermal treatment to modify surface oxygenated groups to obtain different oxygen-doped AC-n. The pre-prepared AC-n was thermally treated in N_2 atmosphere under 400, 600 and 900 °C to obtain AC-n-N400, AC-n-N600 and AC-n-N900, respectively. The AC-n sample was again used as the starting material for nitrogen doping procedure. A mixture of AC-n (5 g), glacial acetic acid (3 ml) and distilled water (50 ml) was stirred for 30 min to obtain a carbon slurry. Urea (3 g), H_2O_2 (10 ml, 10%) and deionized water (30 ml) were added and the solution was stirred for 24 h at room temperature in the dark. Finally, the solution was filtered and calcined at 300, 500 and 700 °C under a nitrogen atmosphere for 1 h, to obtain AC-n-U300, AC-n-U500 and AC-n-U700, respectively.

2.2. Catalyst characterization

N_2 physisorption analysis was carried out in Micromeritics ASAP 2020 instrument at 77 K and the surface area was calculated by Brunauer–Emmett–Teller (BET) method.

X-ray diffraction (XRD) patterns were collected using a X'Pert PRO advanced X-ray diffractometer with $\text{CuK}\alpha$ irradiation ($k = 0.15406$ nm) at 40 kV and 40 mA.

The Raman spectra were recorded using Micro-Raman spectrometer (HORIBA Jobin Yvon) equipped with a 632.81 nm Ar^+ ion laser. The integration time was 20 s for one measurement.

X-ray photoelectron spectroscopy (XPS) analysis was performed by Kratos AXIS Ultra DLD spectrometer with monochromatized aluminum X-ray source (1486.6 eV). The C1s peak at 284.8 eV was taken as references for correcting surface-charging effects.

Temperature programmed desorption (TPD) experiment was carried out in a tubular quartz reactor equipped with a mass spectrometry (QMS 200 Omnistar) for detecting the constitution of the off-gas. For C_2H_2 or HCl-TPD, 75 mg of sample was loaded in the reactor and the in-situ pre-adsorption of C_2H_2 or HCl was achieved by using pure C_2H_2 or HCl, respectively (at 180 °C to pre-adsorption). The inlet gas was then switched to pure Ar with a flow rate of 30 $\text{ml}\cdot\text{min}^{-1}$ for 0.5 h to sweep away physical adsorbed species. C_2H_2 or HCl-TPD was then performed by heating the sample up to 450 °C or 400 °C at a ramp rate of 10 °C $\cdot\text{min}^{-1}$ in the pure Ar atmosphere, respectively. To carry out CO_2/CO -TPD, the sample with a weight of 75 mg also was loaded in the reactor which then was fed with pure Ar with a flow rate of 30 $\text{ml}\cdot\text{min}^{-1}$. The sample was then heated from 30 °C to 900 °C at a ramp rate of 10 °C $\cdot\text{min}^{-1}$ and the temperature was hold at 900 °C for 1 h.

2.3. Catalytic test

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass microreactor (i.d. 10 mm). Acetylene (2.8 $\text{ml}\cdot\text{min}^{-1}$, 0.1 MPa) and hydrogen chloride (3.4 $\text{ml}\cdot\text{min}^{-1}$, 0.1 MPa) were fed through a mixing vessel via calibrated mass flow controllers into a heated glass reactor

containing catalyst (850 mg), with a total C_2H_2 GHSV of 100 h^{-1} . A reaction temperature of 180 °C was chosen. The gas phase products were first passed through an absorption bottle containing NaOH solution and then analyzed on-line by GC equipped with a Porapak N packed column (6 ft \times 1/800 stainless steel) and a flame ionization detector (FID).

3. Results and Discussion

3.1. Textural and chemical properties of oxygen- and nitrogen-doped AC-n

Table 1 shows the surface area and chemical compositions of pristine AC, AC-n, oxygen- and nitrogen-doped AC-n. As anticipated, pristine AC presents a low oxygen content on surface. In order to investigate the effect of oxygen and nitrogen doping on the catalytic performance of AC-n in hydrochlorination of acetylene, liquid phase oxidation using a concentrated HNO_3 solution was carried out to bring substantial oxygen containing groups on surface [32,33]. As can be seen, HNO_3 oxidizing process did introduce a large amount of surface oxygenated groups and also a small amount of nitrogen species which most likely presented in the form of $-\text{NO}_2$ [34]. In addition, it caused a slight decrease of surface area, as a consequence of pore blocking by surface oxygenated groups [35]. HNO_3 treated AC calcined in flowing N_2 under different temperatures showed a similar surface area with pristine AC, demonstrating the decomposing of surface oxygenated groups and relieving pore blocking upon thermal treatment, which also could be seen from the gradual decline of oxygen content with the increasing of temperature. Some works also showed that calcination treatment could recover the surface area of AC-n [32,36]. AC-n-U300 had a relatively low surface area, which might be due to the low calcination temperature, which cannot embed nitrogen into carbon matrix as could be seen from the relatively low nitrogen doping content, and the blockage in pores by unreacted residual urea. AC-n-U500 and AC-n-U700 with higher calcination temperatures showed similar surface areas with pristine AC, demonstrating that the complete decomposing of urea during doping process. AC-n-U700 presented the lowest nitrogen content among the nitrogen-doped samples, which might be due to higher calcination temperature that would easier lead to the decomposition of nitrogen species [37,38].

Table 1
Surface area and chemical compositions of oxygen- and nitrogen-doped AC-n

Sample	Surface area ^① / $\text{m}^2\cdot\text{g}^{-1}$	Surface composition ^② /%		
		C	O	N
AC	1116.86	96.30	3.70	–
AC-n	1076.51	89.05	10.70	0.25
AC-n-N400	1031.09	90.28	9.68	0.04
AC-n-N600	1107.13	90.57	9.40	0.03
AC-n-N900	1055.79	92.00	7.96	0.04
AC-n-U300	975.31	88.65	8.85	2.50
AC-n-U500	1082.38	87.46	8.50	4.04
AC-n-U700	1154.59	90.64	7.16	2.20

^① Determined by nitrogen adsorption and desorption (BET).

^② Determined by XPS analysis.

3.2. The effect of oxygen doping on the performance of oxygen-doped AC-n

Fig. 1 shows the conversions of acetylene over oxygen-doped AC-n. As can be seen from Fig. 1, those catalysts subjected to the thermal treatment in N_2 atmosphere under different temperatures present similar catalytic performances in terms of activity and stability. The conversion of acetylene less than 25% is observed in the gas phase for all the catalysts.

In order to investigate the effect of oxygen doping on the performance of AC-n, AC-n with different amounts and types of surface oxygenated groups should firstly be obtained. Fig. 2 shows the TPD-MS profiles of oxygen-doped AC-n. As can be seen, four oxygen-doped

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