available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Wheat flour-derived N-doped mesoporous carbon extrudes as an efficient support for Au catalyst in acetylene hydrochlorination

Jie Liu, Guojun Lan, Yiyang Qiu, Xiaolong Wang, Ying Li *

Institute of Industrial Catalysis, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, China

ARTICLE INFO

Article history:

Received 6 April 2018

Accepted 19 May 2018

Published 5 October 2018

Keywords:

Au catalyst

Mercury free catalyst

Acetylene hydrochlorination

N doped mesoporous carbon

ABSTRACT

We recently reported an N-doped mesoporous carbon (N-MC) extrudate, with major quaternary N species, prepared by a cheap and convenient method through direct carbonization of wheat flour with silica, which has excellent catalytic performance in acetylene hydrochlorination. Herein, we examined the activity of Au supported on N-MC (Au/N-MC) and compared it with that of Au supported on nitrogen-free mesoporous carbon (Au/MC). The acetylene conversion of Au/N-MC was 50% at 180 °C with an acetylene space velocity of 600 h⁻¹ and $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2}$ of 1.1, which was double the activity of Au/MC (25%). The introduced nitrogen atoms acted as anchor sites that stabilized the Au³⁺ species and inhibited the reduction of Au³⁺ to Au⁰ during the preparation of Au/N-MC catalysts.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Hydrochlorination of acetylene has received significant attention during the past decade as an alternative pathway for the synthesis of vinyl chloride monomer (VCM) [1]. Carbon-supported mercury chloride (HgCl₂) catalysts are currently the most convenient and practical for hydrochlorination of acetylene, but the poor thermal stability of HgCl₂ limits production capacity and leads to severe environmental problems [2]. Therefore, many efforts have been devoted to the development of more efficient and stable non-mercuric catalysts that are suitable for practical use. Hutchings et al. [3,4] studied more than 30 metal chlorides and found that gold catalysts may be the best replacement for HgCl₂ catalysts in this hydrochlorination process because of their high activity. Since then, Au catalysts have been intensively studied and are considered the most promising substitutes for HgCl₂ catalysts in acetylene hydrochlorination [4,5].

The catalytic performance of supported metal catalysts is greatly dependent on the properties of the support, and it is well established that carbon materials act as good supports because of their surface properties, such as large surface area and good electrical conductivity. Recently, nitrogen-doped carbons have become one of the hotspots for various applications, including oxygen reduction/evolution, hydrogen evolution, and carbon dioxide reduction [6]. Dai et al. [7] showed the benefits of nitrogen promotion in Au catalysts. The enhanced catalytic performance was attributed to electron transfer from polypyrrole to the Au³⁺ center, which increased the adsorption of hydrogen chloride. Dai et al. [8] also found that a mesoporous carbon nitride (MCN)-supported Au catalyst with 0.6 wt% Au loading exhibited an activity similar to that of a commercial active-carbon-supported Au catalyst with 1.0 wt% Au loading. The interaction between the nitrogen atoms and the Au active sites contributed to the enhanced activity of the Au/MCN catalyst. Zhao et al. [9] reported a nitrogen-doped Au/NAC catalyst

* Corresponding author. Tel: +86-571-88320766; Fax: +86-571-88320259; E-mail: liying@zjut.edu.cn

This work was supported by Zhejiang Provincial Natural Science Foundation of China (LY17B030010).

DOI: 10.1016/S1872-2067(18)63109-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 10, October 2018

that exhibited good activity and stability for acetylene hydrochlorination. Zhang et al. [10,11] found that the activity and stability of Ru-based catalysts was greatly increased by using N-doped spherical activated carbon as the support.

Moreover, N-doped carbon materials as non-metal catalysts have shown promising properties for acetylene hydrochlorination [12,13]. The introduction of nitrogen changes the electronic structure of the adjacent carbon atoms to adsorb HCl or C_2H_2 easily, and thereby enhances the catalytic activity over that of nitrogen-free carbon materials. Bao et al. [14] demonstrated a nanocomposite of N-doped carbon derived from silicon carbide (SiC@N-C) that showed excellent performance in acetylene hydrochlorination, with 80% conversion at 200 °C, 30 h⁻¹. In a recent study, Li et al. [15] adopted ZIF-8 as the precursor to synthesize ZIF-derived porous carbon materials for acetylene hydrochlorination. In our recent study, we demonstrated that wheat flour-derived granular N-doped mesoporous carbons could be successfully prepared and used as metal-free catalysts for the efficient production of VCM through acetylene hydrochlorination, with excellent catalytic performance and stability (>85% conversion and >99% vinyl chloride selectivity at 220 °C) [16]. The wheat flour-derived granular N-doped mesoporous carbons have a number of remarkable advantages: (1) highly homogeneous distribution of N within the composite; (2) ease of preparation, cost-effectiveness, and environmental friendliness for upscale syntheses; (3) 3D-shaped open-cell structures with low mass transfer limitation and high surface area. However, these N-doped carbon materials are not satisfactory for practical applications because of their low activity.

As mentioned above, N-doped carbons not only show enhanced catalytic activity in acetylene hydrochlorination, but also improve the dispersion of Au^{3+} and strengthen the interaction between Au^{3+} and the carbon surface. In this study, we applied wheat flour-derived N-doped mesoporous carbon (N-MC) as the support for Au catalysts in acetylene hydrochlorination. These catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption analysis, and X-ray photoelectron spectroscopy (XPS). Our results show that the activity of N-doped mesoporous carbon-supported Au catalyst is higher than that of the nitrogen-free mesoporous carbon-supported Au catalyst.

2. Experimental

2.1. Catalyst preparation

Nitrogen-doped mesoporous carbon (N-MC) was prepared as stated in our previous report [16]. 50.0 g of wheat flour was added to a mortar and ground for 30 min, followed by addition of 12 g of SiO_2 and grinding for another 30 min until the solid powders were mixed well. Following this, 25 mL of deionized water was added into the mortar. The mixture was kneaded into dough and kept at room temperature for more than 0.5 h. Thereafter, extrusions of cylinder-shaped particles with size ϕ 2.5 × 30 mm were prepared using a home-made noodle machine and dried in air at room temperature for 10 h. Following

that, the composite was dried at 110 °C for 8 h. Finally, the precursor was carbonized at 850 °C for 3 h under N_2 flow. The N-carbon-silica composite was then dissolved with 5 wt% hydrofluoric acid, filtered and washed several times with hot water, and dried at 110 °C for 10 h. The procedure yielded ~12.5 g of dried carbon materials. The final size of the cylindrical particles was about ϕ 2.0 × 30 mm because of particle shrinkage due to the dehydrogenation of wheat flour. The obtained particles were crushed into 10–18 mesh size for Au catalyst preparation. For comparison, pure starch was used as the precursor to prepare the nitrogen-free mesoporous carbon, hereafter denoted as MC-St.

The typical preparation procedure of mesoporous carbon via a wet impregnation method was as follows [17]: 2.0 g of SiO_2 was impregnated with 7 mL of aqueous solution containing 4.18 g sucrose and 0.33 g oxalic acid. The composite was dried at 100 °C for 6 h and then at 160 °C for 6 h. Thereafter, the composite was carbonized at 850 °C for 3 h under N_2 flow. The carbon-silica composite was then dissolved with 5 wt% HCl, filtered and washed several times with hot water, and dried at 110 °C for 10 h. The template-free product thus obtained was denoted as MC-Su.

Au catalysts were prepared by incipient wetness impregnation. 1 g $HAuCl_4$ (47.8 wt% Au) was dissolved in 100 mL deionized water to obtain aqueous $HAuCl_4$ solution. The aqueous $HAuCl_4$ solution was added dropwise to the pretreated carbon supports to prepare the catalyst, with a gold loading of 0.25 wt%. After the solution homogeneously mixed with the support, the system was aged at ambient temperature for 12 h and then dried at 120 °C for 12 h. The actual Au loading in the samples was determined by spectrophotometry.

2.2. Measurement of catalytic activities

The catalytic performance was investigated using a fix-bed glass reactor (i.d. of 10 mm). Acetylene (99.9% purity) was passed through concentrated sulfuric acid solution to remove trace impurities. Hydrogen chloride gas (99.9% purity) was dried using 5A molecular sieves. Acetylene (20.0 mL min⁻¹) and hydrogen chloride (22.0 mL min⁻¹) were introduced into a heated reactor containing the catalyst (2.0 mL) through a mixing vessel via calibrated mass flow controllers, giving a C_2H_2 gas hourly space velocity (GHSV) of 600 h⁻¹ at 180 °C. The pressure of C_2H_2 and HCl was 0.06 MPa, and the feed volume ratio of $V_{HCl}/V_{C_2H_2}$ was 1.1. The microreactor was purged with nitrogen to remove water and air before the reaction. The reactor effluent was passed through an absorption bottle containing a sodium hydroxide solution to remove the unreacted hydrogen chloride. The gas mixture was analyzed using a GC-1690F gas chromatograph (GC) equipped with an FID.

2.3. Catalyst characterization

XRD measurements were performed using a Rigaku D/MAX-2500/pc powder diffraction system using $Cu K_{\alpha}$ radiation (40 kV and 100 mA) over the 2θ range 10°–80°. Scanning transmission electron microscopy (STEM) images of the sam-

ples were obtained using an FEI Tecnai G20 instrument.

Nitrogen adsorption isotherms were determined at $-196\text{ }^{\circ}\text{C}$ using a Quantachrome Autosorb-iQ apparatus. The samples were outgassed at $350\text{ }^{\circ}\text{C}$ for 10 h before adsorption measurements. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method for adsorption data at relative pressures ranging from 0.05 to 0.30. The total pore volume was determined from the aggregated mass of N_2 vapor adsorbed at a relative pressure of 0.99. The pore size distribution was calculated from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

Argon temperature programmed desorption analyses were carried out using a self-made TPD instrument. The mass spectra were collected on an on-line Hidden gas analyzer (QIC 20). Prior to analysis, the sample ($\sim 50\text{ mg}$) was placed in a fixed bed of a U-shaped quartz tube located inside an electrical furnace. The temperature was increased at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $100\text{--}850\text{ }^{\circ}\text{C}$, under a flow of Ar (30 mL min^{-1}). The following mass units were monitored simultaneously by a quadrupole mass spectrometer: $m/e = 2, 15, 16, 17, 18, 28$, and 44 amu .

The elemental composition was measured with an elemental analyzer (vario EL, Germany). Thermogravimetric analysis (TGA) of samples was conducted on a TG-DSC simultaneous thermal analyzer. About 15 mg of sample was heated to $800\text{ }^{\circ}\text{C}$ under an air atmosphere with a flow rate of 30 mL min^{-1} and heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

XPS was conducted on a Kratos AXIS Ultra DLD instrument using a $300\text{-W Al K}_{\alpha}$ source. The binding energies were calibrated using the contaminant carbon ($\text{C } 1s\text{ }284.6\text{ eV}$).

3. Results and discussion

3.1. Textural properties

Although it has been demonstrated that N-doped carbon materials have high activity and are promising metal-free catalysts for various applications, including oxygen reduc-

tion/evolution, hydrogen evolution, and carbon dioxide reduction, it is still a challenge to develop and scale up the fabrication of N-doped carbon materials via a facile, green, and low-cost route. Moreover, the characteristic powdery texture of carbon nanomaterials strongly limits their application, particularly in gas- and liquid-phase catalytic processes.

Scheme 1 illustrates the preparation of N-MC from wheat flour and silica spheres (the hard template for mesopores). The dough was made into cylinder-shaped extrudates ($\phi\text{ }2.0 \times 30\text{ mm}$) using a home-made noodle machine. After carbonization at $850\text{ }^{\circ}\text{C}$ under an inert atmosphere and subsequent HF etching to remove the silica templates, the cylindrical shape of the material was well-maintained. This is hard to achieve in other methods and is extremely important for improving acetylene hydrochlorination in fixed-bed reactors.

The porosity of the materials was characterized by nitrogen adsorption and the corresponding isotherms and pore size distributions are shown in Fig. S1. All the isotherms are typical type IV with an H1 hysteresis loop, indicating the presence of mesopores. The pore size distribution was calculated using the BJH method, and it centered at about $9.6\text{--}10.7\text{ nm}$, which also revealed that these starch-derived carbon materials had uniform mesopores. Table 1 provides the synthesis parameters and the porosity information of all the mesoporous carbons. The surface areas of all the samples were the range $650\text{--}884\text{ m}^2\text{ g}^{-1}$, and the pore volumes were in the range $0.7\text{--}1.39\text{ cm}^3\text{ g}^{-1}$. The pore size distributions of all carbons were similar because the template used was the same. However, the surface area of MC-Su was slightly higher than that of MC-St and N-MC. This was probably because of the higher molecular weight of starch compared with that of sucrose, which may have affected the mixing and carbonization processes. However, this small difference in surface area did not have a significant effect on the catalytic performance. Fig. S2 gives the TPD-MS profiles corresponding to MC-Su, MC-St, and N-MC. The amounts of CO_2 and CO desorbed on MC-Su were slightly higher than those on MC-St and N-MC, which was in accordance with the element analysis (Table S1). The crystal structures of MC-Su, MC-St, and

Scheme 1. Preparation of Au catalyst supported on N-doped mesoporous carbon.

Table 1
Properties of Au/MC-Su, Au/MC-St, and Au/N-MC catalysts.

Sample	Carbon supports				Au catalysts			Au crystal size ^d (nm)	XPS fitting		
	N (wt%)	S. A. ^a ($\text{m}^2\text{ g}^{-1}$)	P. V. ^b ($\text{cm}^3\text{ g}^{-1}$)	P. D. ^c (nm)	S. A. ^a ($\text{m}^2\text{ g}^{-1}$)	P. V. ^b ($\text{cm}^3\text{ g}^{-1}$)	P. D. ^c (nm)		Au ⁰ (84.4 eV)	Au ⁺ (85.0 eV)	Au ³⁺ (86.6 eV)
Au/MC-Su	<0.3	884	1.39	9.5	875	1.36	10.5	19	85.6	7.6	6.7
Au/MC-St	<0.3	764	0.72	9.8	736	0.69	10.5	18	78.8	7.7	13.5
Au/N-MC	1.8	650	0.70	11.5	631	0.69	12.2	13	49.8	25.3	24.9

^a Specific surface area was determined using the Brunauer-Emmett-Teller method for adsorption data at relative pressure ranging from 0.05 to 0.30.

^b Total pore volume was determined from the aggregated mass of N_2 vapor adsorbed at a relative pressure of 0.99.

^c Pore diameter was calculated from the desorption branches of the isotherms using the BJH method.

^d Crystal size was calculated based on XRD patterns.

N-MC were analyzed by X-ray diffraction-diffusion (Fig. S3(a)). There were two peaks at 23.8° and 43.8° , which were assigned to the (002) and (101) crystal planes of the graphitic structure in the carbons. These peaks were broad, indicating that these mesoporous carbons had an amorphous-like structure. All the samples showed similar XRD patterns, which indicated that the carbon precursor (starch and sucrose) did not affect the structure of the carbon matrix in the mesoporous carbons. The graphitic structures were further characterized by Raman spectroscopy (Fig. S3(b)). The band centered at 1585 cm^{-1} (G band) was ascribed to the stretching of carbon atom pairs of sp^2 domains (both in aromatic rings and conjugated chains), which represents the ideal graphite structure [18]. The band at 1330 cm^{-1} was ascribed to the disordered graphite microcrystalline edge. The wide band at 2670 cm^{-1} (2D band), was ascribed to the disorder in the c-axis and the formation of turbostratic structures. The intensity ratio of the D and G bands (I_D/I_G) was similar, which indicated that the graphitic degree of MC-Su, MC-St, and N-MC was similar, consistent with the XRD results.

Fig. 1(a) and (b) show the nitrogen adsorption isotherms, and pore size distributions of the Au catalysts supported on MC-Su, MC-St, and N-MC. The physical properties of the various Au catalysts are given in Table 1. The low surface areas and similar pore size distributions suggest that the impregnation of HAuCl_4 did not block the pores of the mesoporous carbon supports. Fig. 1(c) shows the XRD patterns of the different catalysts. The catalysts exhibit a distinct peak located at 38.4° , corresponding to the (111) plane of Au crystals. This indicates that the catalysts contain large Au particles. Upon adsorption of HAuCl_4 on a carbon surface, the released heat of adsorption is sufficient to cause significant reduction of HAuCl_4 to Au^0 , particularly when using H_2O as the impregnation solvent [19]. Previous work demonstrated the successful activation of Au/AC catalysts using conventional aqua regia [20], but this activation procedure is highly corrosive and hazardous, has severe environmental impact, and threatens process safety. Additionally, the challenges associated with handling, recovery,

and disposal of used aqua regia make it impractical for industrial applications [21]. The average particle sizes of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts are 13, 18, and 19 nm, calculated by the Scherrer equation based on the XRD results. This indicates that the introduction of nitrogen atoms dramatically improved the dispersion of Au species. Fig. 2 shows the STEM images and particle size distributions of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts. In Fig. 2, metallic nanoparticles (NPs) with large sizes are seen in the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts. The Au NPs are uniformly dispersed on the N-MC support. As shown in Fig. 2(e) and (f), the average sizes of the Au NPs on Au/N-MC and Au/MC-St are about 14.4 and 19.1 nm, respectively. However, many large Au NPs are observed in Fig. 2(d), indicating significant agglomeration of the Au NPs in the Au/MC-Su catalyst. The average particle size of Au/N-MC is much smaller than these of Au/MC-Su and Au/MC-St, and this is consistent with the XRD results. Researchers found that the activity of the catalyst in the synthesis of vinyl chloride was dependent on the $\text{Au}^{3+}/\text{Au}^+$ species on the surface of these NPs in the catalyst. Although the gold catalysts comprise Au NPs, the surfaces of the Au nanoparticles are successfully activated to $\text{Au}^{3+}/\text{Au}^+$ by HCl, as suggested by Hutchings et al. [22]. Therefore, carbon supported Au nanoparticles catalysts are still active for the acetylene hydrochlorination.

3.2. Catalytic properties

The performance of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts within 30 h on stream were evaluated and are shown in Fig. 3. As shown in Fig. 3(a), the catalytic activity of Au/N-MC is superior to that of Au/MC-Su and Au/MC-St. The acetylene conversion of Au/MC-Su was below 20% at 180°C and space velocity of 600 h^{-1} . The acetylene conversion of Au/MC-St was 25%, which was slightly higher than that of Au/MC-Su. Au/N-MC exhibited acetylene conversion as high as 50%, which was the highest among the three catalysts. This probably resulted from the introduction of nitrogen species. Experi-

Fig. 1. N_2 adsorption-desorption isotherms (a), pore size distribution (b), and XRD patterns (c) of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts.

Fig. 2. STEM images and particle size distributions of the Au/MC-Su (a, d), Au/MC-St (b, e), and Au/N-MC (c, f) catalysts.

Fig. 3. Acetylene conversion (a) and TOF (b) of Au/MC-Su, Au/MC-St, and Au/N-MC in acetylene hydrochlorination. Reaction conditions: 180 °C, 0.1 MPa, 600 h⁻¹.

mental studies and theoretical simulations revealed that the carbon atoms bonded with nitrogen atoms acted as active sites and stimulated notable activity at a low space velocity of 30 h⁻¹, as reported previously [16]. However, at a high space velocity of 600 h⁻¹, the N-MC catalyst displayed relatively poor activity (~8% conversion) in the acetylene hydrochlorination reaction, and much lower conversions were detected in MC-Su (~3%) and MC-St (4%). Although both the nitrogen and Au species in the Au/N-MC catalyst served as active sites, the enhancement of Au/N-MC catalyst compared with Au/MC-St is much higher than that of N-MC catalyst compared with MC-St catalyst. This indicates that the nitrogen introduction not only served as a source of active sites but also improving the catalytic performance of Au species. The intrinsic activities of the catalysts were determined by calculating the TOF values based on the acetylene conversions and the total Au loadings (Fig. 3(b)).

Carbon supports also contributed to acetylene conversion, but quantification of the active sites in carbon was difficult. Therefore, the conversion by carbon supports was subtracted from the total conversions by the Au catalysts to calculate the TOF values based on the Au loadings. The TOF of Au/N-MC was 0.91 s⁻¹, which was superior to that of Au/MC-Su (0.59 s⁻¹) and Au/MC-St (0.74 s⁻¹). In addition, the VCM yield of Au/N-MC in acetylene hydrochlorination was larger than that of the Au catalysts reported in the literature (Table S4).

XPS was subsequently conducted to probe the chemical states of the N elements in the carbon materials. Fig. 4(a) shows the N 1s XPS spectra and fitting results of the N-MC and Au/N-MC catalysts. The XPS spectra of the N-MC and Au/N-MC catalysts were deconvoluted into four peaks ascribed to pyridinic (398.3 ± 0.2 eV), pyrrolic (400.0 ± 0.2 eV), quaternary (401.1 ± 0.2 eV), and oxidized (404.0–405.6 eV) N species [23].

Fig. 4. (a) N 1s XPS spectra of the N-MC and Au/N-MC catalysts; (b) Au 4f XPS spectra of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts.

The fitted analysis data show that the main N species in N-MC is the quaternary nitrogen, which comprises around 65%. The percentage of quaternary nitrogen slightly decreased to 63.4% in the Au/N-MC catalyst (Table S2).

Fig. 4(b) shows the Au 4f XPS spectra and fitting results of the Au/MC-Su, Au/MC-St, and Au/N-MC catalysts. The detailed fitting analysis showed two peaks corresponding to the $4f_{7/2}$ and $4f_{5/2}$ spin-orbit states, for each valence state of the gold species. In accordance with the literature [24,25], the Au $4f_{7/2}$ peaks at 84.4, 85.0, and 86.6 eV were ascribed to Au^0 , Au^+ , and Au^{3+} species, respectively. The Au $4f_{5/2}$ peaks at 87.7, 88.6, and 90.3 eV were ascribed to Au^0 , Au^+ , and Au^{3+} species, respectively. The proportions of Au ions at different oxidation states in the catalysts were calculated from the relative peak areas, and the results are listed in Table 1. The Au^+ species content in the fresh Au/N-MC catalyst was 25.3%, which was higher than that in the Au/MC-Su (7.6%) and Au/MC-St (7.7%) catalysts. The Au^{3+} species content in the fresh Au/N-MC catalyst was 24.9%, which was higher than that in the Au/MC-Su (6.7%) and Au/MC-St (13.5%) catalysts. These results suggest that N atoms inhibited the reduction of Au^{3+} and Au^+ into Au^0 during the preparation. Hutchings et al. [26,27] suggested that the highly dispersed Au^+ species were crucial for this reaction, the oxidized species are responsible for the activity in these catalyst systems, and the activity is related to the $\text{Au}^+-\text{Au}^{3+}$ redox couple. Mechanistically, the reaction could be hypothesized to proceed through the oxidative addition of HCl to Au chloride, followed by the addition of acetylene and reductive elimination of VCM through the $\text{Au}^+-\text{Au}^{3+}$ redox couple. The proportion of the $\text{Au}^+/\text{Au}^{3+}$ species is directly related to the activity for acetylene hydrochlorination. Therefore, the greater difference in the oxidized Au species ratios was probably the main reason for the higher activity of the Au/N-MC catalyst as compared to that of the Au/MC-Su and Au/MC-St catalysts.

Fig. S4 gives the N_2 adsorption isotherms and pore size distributions of the used Au/MC-Su, Au/MC-St, and Au/N-MC catalysts. The specific surface area and total pore volume of the used Au catalysts decreased slightly, as shown in Table S3. TGA was carried out in an air atmosphere to measure the amount of carbon deposition, and the results are shown in Fig. S5. The negligible coke deposition and the small decrease in the ratio of surface area of the used catalysts to fresh catalysts suggest that carbon deposition is not the main reason for the deactivation of Au-based catalysts. The stability of Au/N-MC catalyst was further tested under the conditions of 180 °C and 50 h^{-1} GHSV over 100 h. The results are shown in Fig. 5. The Au/N-MC catalyst showed excellent stability, with an acetylene conversion of 80% at a C_2H_2 hourly space velocity of 50 h^{-1} , which decreased slightly to 78% after 60 h's reaction. These results indicated that the Au/N-MC catalyst exhibited favorable activity and stability, and that the presence of a significant fraction of N species

Fig. 5. Long-term stability test of Au/N-MC in acetylene hydrochlorination. Reaction conditions: 180 °C, 0.1 MPa, 50 h^{-1} .

was essential for enhancing both the activity and stability of Au-based catalysts. The excellent performance will make this catalyst attractive for both fundamental research and practical applications.

4. Conclusions

In summary, N-doped mesoporous carbons were prepared by using wheat flour as both the carbon and nitrogen source and used as supports for Au catalysts in acetylene hydrochlorination. The Au/N-MC catalyst exhibited higher activity in the hydrochlorination of acetylene than did the Au/MC-Su and Au/MC-St catalysts. At 180 °C with a space velocity 600 h⁻¹ and $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2} = 1.1$, the acetylene conversion was 50%. The nitrogen species anchored the gold cations and consequently stabilized the gold catalysts. The excellent performance of the Au/N-MC catalyst demonstrated its potential as an alternative to mercury chloride catalysts for acetylene hydrochlorination. The wheat flour-derived N-doped mesoporous carbons, owing to their easy and cheap upscale synthesis, open new avenues toward the development of alternative and sustainable catalytic materials with a wide range of practical applications beyond the reactions targeted in this study.

References

- [1] H. Schobert, *Chem. Rev.*, **2014**, 114, 1743–1760.
- [2] M. Y. Zhu, Q. Q. Wang, K. Chen, Y. Wang, C. F. Huang, H. Dai, F. Yu, L. H. Kang, B. Dai, *ACS Catal.*, **2015**, 5, 5306–5316.
- [3] G. J. Hutchings, *J. Catal.*, **1985**, 96, 292–295.
- [4] C. J. Davies, P. J. Miedziak, G. L. Brett, G. J. Hutchings, *Chin. J. Catal.*, **2016**, 37, 1600–1607.
- [5] P. Johnston, N. Carthey, G. J. Hutchings, *J. Am. Chem. Soc.*, **2015**, 137, 14548–14557.
- [6] Y. L. Cao, S. J. Mao, M. M. Li, Y. Q. Chen, Y. Wang, *ACS Catal.*, **2017**, 7, 8090–8112.
- [7] X. Y. Li, M. Y. Zhu, B. Dai, *Appl. Catal. B*, **2013**, 142, 234–240.
- [8] B. Dai, X. Y. Li, J. L. Zhang, F. Yu, M. Y. Zhu, *Chem. Eng. Sci.*, **2015**, 135, 472–478.
- [9] J. Zhao, J. T. Xu, J. H. Xu, T. T. Zhang, X. X. Di, J. Ni, X. N. Li, *Chem. Eng. J.*, **2015**, 262, 1152–1160.
- [10] L. J. Hou, J. L. Zhang, Y. F. Pu, W. Li, *RSC Adv.*, **2016**, 6, 18026–18032.
- [11] N. Xu, M. Y. Zhu, J. L. Zhang, H. Y. Zhang, B. Dai, *RSC Adv.*, **2015**, 5, 86172–86178.
- [12] X. Y. Li, Y. Wang, L. H. Kang, M. Y. Zhu, B. Dai, *J. Catal.*, **2014**, 311, 288–294.
- [13] Y. Yang, G. J. Lan, X. L. Wang, Y. Li, *Chin. J. Catal.*, **2016**, 37, 1242–1248.
- [14] X. Y. Li, X. L. Pan, L. Yu, P. J. Ren, X. Wu, L. T. Sun, F. Jiao, X. H. Bao, *Nat. Commun.*, **2014**, 5, 3688.
- [15] S. L. Chao, F. Zou, F. F. Wan, X. B. Dong, Y. L. Wang, Y. X. Wang, Q. X. Guan, G. C. Wang, W. Li, *Sci. Rep.*, **2017**, 7, 39789.
- [16] G. J. Lan, Y. Wang, Y. Y. Qiu, X. L. Wang, J. Liang, W. F. Han, H. D. Tang, H. Z. Liu, J. Liu, Y. Li, *Chem. Commun.*, **2018**, 54, 623–626.
- [17] Z. L. Jiang, G. J. Lan, X. Y. Liu, H. D. Tang, Y. Li, *Catal. Sci. Technol.*, **2016**, 6, 7259–7266.
- [18] W. Jiang, Y. Li, W. F. Han, Y. P. Zhou, H. D. Tang, H. Z. Liu, *J. Energy Chem.*, **2014**, 23, 443–452.
- [19] M. Conte, C. J. Davies, D. J. Morgan, T. E. Davies, D. J. Elias, A. F. Carley, P. Johnston, G. J. Hutchings, *J. Catal.*, **2013**, 297, 128–136.
- [20] M. Conte, C. J. Davies, D. J. Morgan, A. F. Carley, P. Johnston, G. J. Hutchings, *Catal. Lett.*, **2014**, 144, 1–8.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1664–1671 doi: 10.1016/S1872-2067(18)63109-2

Wheat flour-derived N-doped mesoporous carbon extrudes as an efficient support for Au catalyst in acetylene hydrochlorination

Jie Liu, Guojun Lan, Yiyang Qiu, Xiaolong Wang, Ying Li *
Zhejiang University of Technology

Wheat flour-derived N-doped mesoporous carbon extrudes were prepared by a cheap and convenient method as excellent supports for Au-based mercury-free acetylene hydrochlorination catalysts.

- [21] J. Zhao, B. Wang, X. Xu, Y. Yu, S. Di, H. Xu, Y. Zhai, H. He, L. Guo, Z. Pan, X. Li, *J. Catal.*, **2017**, 350, 149–158.
- [22] B. Nkosi, M. D. Adams, N. J. Coville, G. J. Hutchings, *J. Catal.*, **1991**, 128, 378–386.
- [23] S. G. Zhang, S. Tsuzuki, K. Ueno, K. Dokko, M. Watanabe, *Angew. Chem. Int. Ed.*, **2015**, 54, 1302–1306.
- [24] C. F. Huang, M. Y. Zhu, L. H. Kang, X. Y. Li, B. Dai, *Chem. Eng. J.*, **2014**, 242, 69–75.
- [25] X. Liu, M. Conte, D. Elias, L. Lu, D. J. Morgan, S. J. Freakley, P. Johnston, C. J. Kiely, G. J. Hutchings, *Catal. Sci. Technol.*, **2016**, 6, 5144–5153.
- [26] G. Malta, S. A. Kondrat, S. J. Freakley, C. J. Davies, L. Lu, S. Dawson, A. Thetford, E. K. Gibson, D. J. Morgan, W. Jones, P. P. Wells, P. Johnston, C. R. A. Catlow, C. J. Kiely, G. J. Hutchings, *Science*, **2017**, 355, 1399–1402.
- [27] G. Malta, S. J. Freakley, S. A. Kondrat, G. J. Hutchings, *Chem. Commun.*, **2017**, 53, 11733–11746.

小麦粉衍生中孔氮掺杂颗粒炭负载金催化剂用于乙炔氢氯化反应

刘 杰, 蓝国钧, 邱一洋, 王小龙, 李 璘*

浙江工业大学工业催化研究所, 浙江杭州310032

摘要: 聚氯乙烯是五大工程塑料之一, 在国民经济中占有重要的地位。基于中国富煤少油缺气的能源格局, 我国主要采用基于煤化工的电石法氯乙烯生产工艺, 但该工艺必须采用氯化汞催化剂, 受到国际限汞公约的影响, 无汞催化剂的开发迫在眉睫。其中炭负载金催化剂在该反应中活性最高, 近几年来取得了较大进展, 有望实现产业化。

氮掺杂的炭材料在诸多反应中展现了较好的性能, 其负载金属催化剂可以有效提高金属的分散度及稳定性, 成为近几年多相催化领域的一个研究热点。最近我们课题组报道了一种氮掺杂中孔成型的制备方法: 以小麦粉为原料, 通过直接炭化法制备了氮掺杂中孔成型炭, 这种氮掺杂中孔成型炭作为无汞催化剂在乙炔氢氯化反应中显示出了优异的催化性能。小麦粉衍生的氮掺杂中孔成型炭具有成型容易、原料价廉易得、易于放大生产等优点, 是优选的工业化催化剂的载体。

本文以这种氮掺杂的成型炭为载体制备了负载型金催化剂, 研究其催化乙炔氢氯化性能。结果表明, 氮的掺杂使得中孔炭负载金(Au/N-MC)催化剂上乙炔氢氯化活性明显提高。在氯化氢/乙炔比例1.1、反应温度180 °C、乙炔空速600 h⁻¹的条件下, Au/N-MC上的乙炔转化率为50%, 是Au/MC催化剂活性的2倍。通过对催化剂的表征发现, 氮的掺杂能有效地锚定Au/N-MC催化剂中活性组分Au³⁺, 抑制催化剂制备过程中Au³⁺还原为Au⁰, 从而提高催化剂活性和稳定性。小麦粉衍生的氮掺杂中孔炭的原料价廉易得, 生产工艺简单, 易成型, 也容易实现工业化生产, 是负载型金属催化剂的优良载体, 其负载的无汞催化剂性能优越, 有望取代电石法氯乙烯产业的汞催化剂, 成为新一代无汞催化剂。

关键词: 金催化剂; 无汞催化剂; 乙炔氢氯化; 氮掺杂中孔炭

收稿日期: 2018-04-06. 接受日期: 2018-05-19. 出版日期: 2018-10-05.

*通讯联系人. 电话: (0571)88320766; 传真: (0571)88320259; 电子信箱: liying@zjut.edu.cn

基金来源: 浙江省自然科学基金(LY17B030010).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).