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Boron-modified activated carbon supporting low-content Au-based catalysts for acetylene hydrochlorination

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ABSTRACT

A series of boron-modified low-gold-content Au-based catalysts were prepared by impregnation. Characterization by N_2 adsorption/desorption, XPS, H_2–TPR, HCl/C_2H_2–TPD, TG, TEM, and SEM was applied to analyze the catalyst. Compared with the unmodified catalyst, B-modified Au0.25%/BAC-20% exhibited better performance (acetylene conversion increase by 21.4% and selectivity to VCM of more than 99.5%) at a space velocity of 770 h^{-1} and 150 °C. The results indicated that the presence of boron species is favorable to the stabilization of catalytically active Au^{3+} species and the inhibition of Au^{3+} to Au^0 during acetylene hydrochlorination, and hence improves the catalytic stability. In addition, the presence of boron species can effectively inhibit carbon deposition and also inhibit the catalyst sintering during the reaction. TPD experiments revealed that not the adsorption ability of C_2H_2 but the adsorption ability of the HCl played a crucial role in boron-modified Au-based catalysts.

1. Introduction

Polyvinylchloride (PVC), as one of the top five engineering plastic materials in the world, is widely used in the chemical industry [1,2]. Being the main monomer of PVC, vinyl chloride monomer (VCM) can be manufactured by various processes based on ethylene and acetylene, as well as ethane. Although they have largely been superseded by the ethylene method in many countries, rises in energy costs present an opportunity for coal-based processes to become increasingly financially competitive in China, which makes the coal-based manufacture of vinyl chloride through acetylene hydrochlorination method a promising route [3]. However, the acetylene hydrochlorination process utilizes carbon-supported 10–14% $HgCl_2$ as a conventional catalyst, which results in severe environment pollution. What is worse, mercury vapor mixed with the VCM during the reaction could seriously impair the product quality. The above drawbacks greatly restrict the sustainable development of the acetylene process [4]. The Minamata Convention on Mercury was reached by more than 140 countries in 2013, aiming to gradually reduce the production and trade of Hg-containing products before 2020. The Chinese government promised to cut the consumption of Hg in the PVC industry by 2020 and prohibit its use step by step [5]. Therefore, the development of environmentally friendly mercury-free catalysts has become one of the priorities of the calcium carbide PVC industry [2–7].

In 1975, Shinoda investigated the activity of a wide range of carbon-supported metal chloride catalysts for acetylene hydrochlorination and correlated their activity with the electron affinity of the metal cation, divided by the metal valence [8]. Subsequently, in 1985, Hutchings et al. used more than 20 kinds of metal components for acetylene hydrochlorination and found that the activity of components correlated with the standard electrode potential of the cations, with the following order of initial activity: $Pd^{2+} > Hg^{2+} > Cu^{2+}$, $Cu^{+} > Ag^{+}$. Later, they also studied in detail the activated carbon-supported gold catalysts Au/C and found that gold had high activity in the acetylene hydrochlorination reaction [2,9]. Since then, supported Au catalysts for acetylene hydrochlorination have drawn more and more attention. In 2008, Marco Conte et al. reported that the incorporation of Pd into Au could improve the initial catalytic activity; however, it leads to lower vinyl chloride selectivity. Furthermore, carbon deposits could result in catalyst deactivation [1]. In 2012, Haiyang Zhang et al. reported that incorporation of La was favorable to inhibition of carbon deposits [10]. In 2013, Xiaoyan Li et al. reported that PPY carbon nanotubes could enhance the adsorption of HCl onto catalyst during the reaction process, which improved the catalytic activity [4]. Marco Conte et al. reported that with processing by aqua regia, Au nanoparticle dispersion on catalysts could be improved; at the same time, the number of oxygen-containing functional groups on the catalyst increased [11]. In 2014, Haiyang Zhang reported an Au—Co—Cu/SAC catalyst and forecast that the lifespan of the catalyst could reach 6513 h [12]. Chaofeng Huang reported a TiO_2–Au/AC supported catalyst and found that the interaction

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between TiO_2 and Au could improve the adsorption of HCl onto the catalyst, improving the catalyst stability [13]. Jia Zhao et al. reported a nitrogen-doped Au/NAC catalyst that exhibited good catalytic activity and stability in acetylene hydrochlorination. Besides, the presence of nitrogen could effectively inhibit the reduction of Au^{3+} to Au^0 [14]. Recently, Zhang et al. found that the catalytic activity of the N-doped AC catalyst for acetylene hydrochlorination depended strongly on the various nitrogen species, in the sequence pyrrolic N > graphitic N > pyridinic N. On the basis of the TPD experiments, a positive correlation between the pyrrolic N content and the capability for adsorbing hydrogen chloride and acetylene was obtained [15]. Dai and co-workers reported that over the B, N-G catalyst (without Au present), the initial acetylene conversion is about 95% at 150 °C and 36 h^{-1} within 240 min. Density functional theory calculations and temperature-programmed desorption results indicate that the synthetic effect of B and N doping can promote HCl adsorption, which is the rate-determining step in acetylene hydrochlorination [16]. Jia Zhao et al. reported that with Au1InIII4CsI/AC catalyst, the conversion of acetylene reached more than 92.8%, and there was only 3.7% C_2H_2 conversion loss after running for 50 h under the reaction conditions of temperature 180 °C and C_2H_2 hourly space velocity of 1480 h^{-1}. Zhang et al. reported that the $Ba^{(II)}$ additive could inhibit the occurrence of coke deposition on the catalyst surface and inhibit catalyst sintering [17]. Bao et al. reported that a nanocomposite of N-doped carbon derived from silicon carbide (SiC@N–C) directly activates acetylene hydrochlorination; has stable activity during acetylene conversion, which can reach 80%; and has vinyl chloride selectivity >98% at 200 °C [18]. Yanzhao Dong et al. reported that the addition of Sn could inhibit the transformation of Au^{3+} to Au^0, which, as a consequence, improved the catalytic activity and stability [19]. It is worth pointing out that in most of the above reports, the gold content is 1%, which is too high to make it an available catalyst for industrial application. On the basis of the application reality, our team has been carrying out a lot of work on low-gold-content catalysts for acetylene hydrochlorination and further studying the catalytic mechanism. After much careful and meaningful work, we have developed a well-performing low-gold-content catalyst with a selectivity of 97.4%, which is comparable to that of 1% gold-content catalyst [20].

As mentioned above, higher gold content and the reduction of Au^{3+} to Au^0 are the two major remaining obstacles to the improvement of catalytic activity and stability [21,22]. Our recent work has found that B-doped catalysts could obviously improve the catalyst performance with gold content as low as 0.25%. Although there are many reports that the properties of carbon materials can be improved through the doping of heteroatoms such as nitrogen and boron [23–25], which suggest that doping is an effective method of improving the properties of carbon materials, there are few reports on the study of B-doped catalysts for acetylene hydrochlorination as yet. These advances motivate us to study the doping of activated carbon by boron. Here, we report a new supported catalyst. The support (activated carbon) is modified by boron, which could change the electronic properties of the activated carbon, resulting in better catalytic activity and stability with gold content as low as 0.25%. The results revealed that at 150 °C with space velocity 770 h^{-1} and $V_{HCl}/V_{C2H2} = 1.15$, the acetylene conversion could reach 81.47% and the vinyl chloride selectivity could be higher than 99%.

2. Experimental

2.1. Materials

Granular activated carbon and H_3BO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd.; $HAuCl_4{\cdot}4H_2O$ (1 g) and absolute ethanol were purchased from Tianjin Sailboat Chemical Reagent Co., Ltd.; C_2H_2 (gas, >99%) and HCl (gas, 99.99%) were obtained from Dalian Special Gas Co. All the materials and chemicals were commercially available and were used without further purification. The water used in all the experiments was deionized.

2.2. Catalyst preparation

B-doped activated carbon (AC) was prepared based on the modified process described below. AC was initially washed with HNO_3 solution (65 wt.%) at room temperature for 2 h. The obtained activated carbon was then filtered and washed with distilled water and dried at 100 °C for 12 h (sample AC). A mixture of AC (6 g), boric acid (1.5 g), and distilled water (50 mL) was stirred until the impregnation liquid evaporated at 60 °C. Finally, the sample was desiccated and calcined at 500 °C under nitrogen for 5 h. The obtained sample was labeled as BAC-20%, where BAC represents "boron-doped AC" and 20% is the weight percentage of boric acid in the modified support. Similar methods were used to prepare BAC catalysts labeled as BAC-22%, BAC-18%, BAC-14%, and BAC-10%.

Supported Au catalysts were prepared using an incipient wetness impregnation technique. A $HAuCl_4{\cdot}4H_2O$ (assay: 49.7%) solution in absolute ethanol was added dropwise to the BAC or AC1 support with agitated stirring to obtain a catalyst with a final Au loading of 0.25 wt.%. The sample was impregnated for 12 h and then dried for 12 h at 140 °C. The obtained catalysts were denoted as Au 0.25%/BAC-10%, Au 0.25%/BAC-14%, Au 0.25%/BAC-18%, Au 0.25%/BAC-20%, and Au0.25%/BAC-22%.

2.3. Characterization

Low-temperature N_2 adsorption/desorption (BET) experiments were conducted using a Quantachrome NOVA4200e surface area and pore size analyzer with 99.999% N_2 as absorption gas. The samples were first degassed at 150 °C for 2 h and then analyzed via liquid nitrogen adsorption at −196 °C. X-ray diffraction (XRD) analysis of the catalysts was carried out on a D8ADVANCE X-ray diffractometer using a Cu Kα radiation source ($\lambda = 0.1541$ nm) with a step size of 0.01° 2θ from 10° to 85°. Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments were performed using a Quantachrome Chembet Pulsar adsorption instrument equipped with a thermal conductivity detector (TCD). The weight of all samples for TPR and TPD experiments was 0.1 g. For TPR experiments, the samples were treated with He gas at 150 °C for 1 h. After cooling, the temperature was increased from room temperature to 600 °C at a heating rate of 10 °C min^{-1} with a 5 vol.% H_2/N_2 atmosphere flowing at a rate of 100 ml min^{-1}. The desorption of moisture was performed at 200 °C for 120 min before the TPD experiment. For C_2H_2 and HCl TPD experiments, the adsorption experiments of samples were performed at 90 °C for 30 min, flushed with a 20 ml min^{-1} pure C_2H_2 or HCl gas. After adsorption, the samples were treated with pure He gas at 90 °C for 60 min and then cooled to room temperature. After that, desorption was performed from 30 to 600 °C under helium. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on an ESCALABMKLL spectrometer (VG, England) using Al Kα X-ray radiation (150 W, 15 kV). During data processing of the XPS spectra, binding energy values were referenced to the C1*s* peak (284.6 eV) from the adventitious contamination layer. Sample morphology was observed with a transmission electron microscope (TEM) (FEI, Tecnai G2 F20 S-Twin) operated at 200 kV. Samples were dispersed in alcohol in an ultrasonic bath and a drop of supernatant suspension was poured onto a holey-carbon-coated grid and dried completely before the measurements were taken.