

Trimetallic Au-Cu-La/AC for Acetylene Hydrochlorination in a Multi-Tubular Fixed Bed Reactor

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ABSTRACT: The metal chloride of LaCl_3 was chosen to modify the Au-Cu/AC to decrease the noble metal of gold and enhance the catalytic performances. Then a mercury-free catalyst of Au-Cu-La/AC was prepared by the impregnation method, and the fresh Au-Cu-La/AC and Au-Cu/AC catalysts were also characterized in comparison. The catalytic performances of mercury-free catalysts for acetylene hydrochlorination were carried out for 3500 hours in a multi-tubular fixed bed reactor. The additives of La can make the active species dispersed well and retard the aggregation of particles. And the acetylene conversion rate remained stable over 98.5% with the fluctuations, less than 1%, and the selectivity of vinyl chloride maintained the stability of 99% or higher, which indicated that the mercury-free catalyst has excellent catalytic performances for acetylene hydrochlorination.

KEYWORDS: Mercury-free catalyst; Acetylene hydrochlorination; La; Gold; Multi-tubular fixed bed reactor

INTRODUCTION

Acetylene hydrochlorination is one of the main processes for the commercial production of Vinyl Chloride Monomer (VCM), providing the most important raw material for PVC production in coal-rich areas, especially

in China, accounting for 70% of total PVC production [1]. Left and right, although this method has been largely replaced by vinyl processes in many other countries. It is known that industrial catalysts previously used in this

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process are rapidly deactivated [2] due to the loss of volatile active components in toxic HgCl_2 complexes, and sublimation of mercury [3] leads to serious safety and environmental problems. According to the latest Minamata Convention signed in Japan, the Governing Council of the United Nations Environment Programme will ban the use of mercury chloride in 2020 [4]. Therefore, more effective catalysts for this technology must be developed by using coal as starting material. Various new noble metal chloride catalysts, including AuCl_3 , PtCl_4 , PdCl_2 , or RuCl_3 , have been tested and developed, as reported in the literature [5-10]. In last decade, Au-based catalysts have already been studied in detail and a supported Au-based catalyst with excellent catalytic performance in acetylene hydrochlorination reaction has been applied [11-13].

Whereas, it was found that the reduction of Au^{3+} (as an active site) to Au^0 and subsequent sintering resulted in poor distribution of Au particles on the carbon support and rapid loss of activity⁹. Therefore, in most literature, the loading of gold on the catalyst is greater than 1 wt%. In order to alleviate this problem, some other metals are doped into the Au catalyst to form a bimetallic Au-based catalyst [14]. Gold and another metal containing bimetallic catalysts can provide improved performance through their synergetic effect in the acetylene hydrochlorination reaction. The mixed metal ions were selected from Ru^{3+} , La^{3+} , Ir^{3+} , Pd^{2+} , Pt^{4+} , Rh^{3+} , Cu^{2+} or Co^{3+} [15-20]. However, to date, the reported Au-based catalysts have not been available in industrial PVC manufacturing due to the high price of Au and the relative short lifetime of the catalysts. Generally, the reason behind the deactivation of catalysts is identified as Au^{3+} reduction and oligomer formation [18, 19]. Alloying Au with other base metals is a promising way to improve the catalytic activity and a bimetallic Au-Cu/AC catalyst showed promising catalytic activity and acetylene conversion is 99.5% at 200 h [15]. Au-based catalysts have attracted the attention of many researchers [21-24], but most of them focused on the activity of multi-metallic catalyst, while the research on the deactivation of Au-based catalysts and the role of non-noble metals is insufficient [18].

In this work, the effects of LaCl_3 additives on the performances of Au-Cu/AC catalysts were investigated to improve the activity and the stability of a relative

cheap catalyst for acetylene hydrochlorination. Further the catalytic performances of Au-Cu-La/AC with a long-run test of 3500 hours were carried out for acetylene hydrochlorination in a multi-tubular fixed bed reactor.

EXPERIMENTAL SECTION

Catalyst Preparation

The gold-based catalysts were prepared by a wetness impregnation technique using the precursors involving HAuCl_4 , CuCl_2 and /or one of the chloride of Ce, K and Ni. Activated carbon (AC 8-12 mesh, Coconut shell, from Shanghai Xinhui activated carbon Co., Ltd.) was washed by a dilute aqueous HCl solution (1.5mol/L) at 65°C for 4 h with to remove impurities, which were poisons for the hydrochlorination reaction, followed by washing with deionized water to neutral pH and desiccating at 120°C for one day, then the obtained activated carbon (AC) as the support. Bimetallic Au-Cu/AC catalyst was prepared by impregnating quantitatively the obtained clean AC support with an aqueous solution of HAuCl_4 and CuCl_2 at 353 K under stirring for 3 h, then the obtained mixture was desiccated at 150°C for 12 h. For convenience, the Au-Cu/AC catalyst with the gold loading amount of 0.5 wt% and 0.2% was labeled as 4Au-Cu/AC and Au-Cu/AC, respectively. When one of the chloride of Ce, K and Ni was added quantitatively into the aqueous solution of HAuCl_4 and CuCl_2 , the trimetallic catalysts of Au-Cu-Ce/AC, Au-Cu-K/AC or Au-Cu-Ni/AC can be prepared through the above similar procedure. The Au loading of the catalyst fixed at 0.2 wt% unless mentioned, and the non-noble gold was fixed at 2.5%, respectively.

Catalyst characterization

The absolute content of gold in all catalysts was measured with inductively coupled plasma-atomic emission spectrometry (ICP-AES)(710ES, Varian Company in USA). The pore size distribution and specific surface areas of the catalysts were analyzed by ASAP2020 surface area and porosity analyzer to conduct low temperature N_2 adsorption/desorption experiments. The catalysts were heated at 300°C and outgassed for 3 h at this temperature under high vacuum and measured using liquid nitrogen adsorption at -196°C. XRD data was collected by using a Bruker D8 advanced X-ray diffract meter with $\text{Cu-K}\alpha$ irradiation at 40 kV and 40 mA

in the scanning range from 10° to 80°. Transmission electron microscopy was conducted using a JEM 2100F TEM. The samples were dispersed in ethanol and supported on carbon film coated copper grids before the characterization of TEM.

Catalytic tests

The catalytic performance in acetylene hydrochlorination was evaluated in a 10 ml catalyst loaded fixed-bed micro-reactor (diameter 10 mm) under the pressure of 0.1 MPa and temperature of 165 °C. The reactor was firstly purged with nitrogen to remove water in the reaction system. Hydrogen chloride was then passed through the reactor at a flow rate of 50 ml/min for 2 h to activate the catalyst. After the reactor was heated to 165 °C, acetylene and hydrogen chloride were sent in at a flow rate of 20 and 22 mL/min respectively.

The reaction product was analyzed by gas chromatography (GC-920, Al₂O₃ PLOT column). The catalyst activity was measured by the conversion of acetylene ($X_{C_2H_2}$) and selectivity of VCM (S_{VCM}) as follows:

$$X_{C_2H_2} = (1 - \Phi_{C_2H_2}) \times 100\% \quad (1)$$

$$S_{VCM} = \Phi_{VCM} / (1 - \Phi_{C_2H_2}) \times 100\% \quad (2)$$

Where $\Phi_{C_2H_2}$ is of residual volume fraction of acetylene and Φ_{VCM} the volume fraction of chloroethylene.

RESULTS AND DISCUSSIONS

Effects of metal additives on the performance of Au-Cu/AC catalysts

Mercury-free catalyst of 4Au-Cu/AC with Au loading of 0.5 wt% gave excellent performance with more than 99.5% C₂H₂ conversion and VCM selectivity which did not decline in 200 h on stream¹⁵. In the present study, the loading amount of Au on the catalyst of Au-Cu/AC was decreased from 0.5 wt% to 0.2 wt%, reducing about 40%. Then several metal additives which showed acetylene hydrochlorination reaction activity and stability was adopted to improve the catalytic performance of Au-Cu/AC catalyst. The loading amount of metal additives was 2.5 wt%, which was the same as the loading amount of Cu. Fig.1 displays the effect of metal additives on the catalytic performance of Au-Cu/AC catalyst.

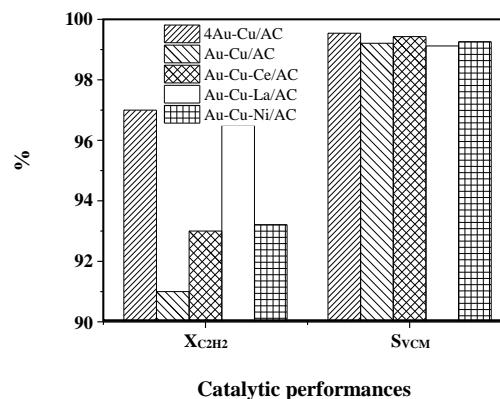


Fig. 1: Effect of metal additives on the catalytic performance of Au-Cu/AC catalyst

It can be seen that the noble metal of Au is reduced by about 40%, the conversion of acetylene is reduced from 97% to 91%, and the metal additive (Ce, La, Ni) is increased. Among these metal additives, the acetylene conversion achieves the highest value of 96.5% over Au-Cu-K/AC catalysts, which is very close to the 4Au-Cu/AC. Meanwhile all these related catalysts show the selectivity to VCM above 99.0%. It was clear that the trimetallic catalyst Au-Cu-La/AC shows the superior activity and stability for acetylene hydrochlorination.

Characterization of Au-Cu-La/AC

Catalyst texture properties

The porous structure parameters of activate carbon (AC), fresh Au-Cu /AC and Au-Cu-La /AC catalysts were listed in Table 1. After the wetness impregnation, it could be seen that the surface area (S_{BET}) of Au-Cu-La/AC catalyst and Au-Cu/AC decreased from 1038 m²/g to 960 m²/g and 980 m²/g, meanwhile, the volume pores (V_p) and the average pore diameter (D_p) also decreased. This means that metal loading on the active carbon had been formed.

Effect of the additives on the dispersion of active species

Fig 2a and b displayed the XRD patterns of the fresh Au-Cu/AC, fresh Au-Cu-La/AC catalysts. Besides the amorphous diffraction peaks of carbon, no discernible reflection is detected in the fresh catalysts. The results show that the active catalysts in the fresh catalysts with the additives of Cu and La are more dispersed, and the high dispersibility of the active materials can be well maintained.

Table 1: Porous structure parameters of mercury-free catalysts.

Sample	$S_{\text{BET}}, (\text{m}^2 \cdot \text{g}^{-1})^{\text{a}}$	$V_{\text{p}}, (\text{cm}^3 \cdot \text{g}^{-1})^{\text{b}}$	$D_{\text{p}}, (\text{nm})^{\text{c}}$
Active carbon (AC)	1038	0.415	2.07
Fresh Au-Cu/AC	980	0.391	1.92
Fresh Au-Cu-La/AC	960	0.366	1.97

^aBET specific surface area; ^bBJH volume of pores; ^cAverage pore diameter

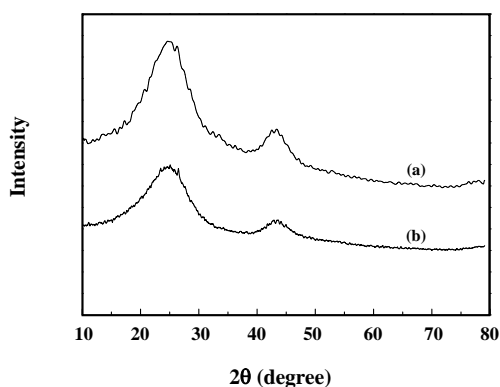


Fig. 2: The XRD patterns of catalysts: (a) fresh Au-Cu /AC; (b) fresh Au-Cu-La/AC.

Fig. 3 displayed the TEM images of the fresh Au-Cu/AC, fresh Au-Cu-La/AC catalysts. It was confirmed that the catalyst has numerous particles with the particle size of several nanometers from the TEM image in Fig.3.

The loading amounts of the metal additives

Certain amount of fresh and used catalyst in the crucible was placed in a furnace at 800°C for 5 hours, and the roasted residues was dissolved in the aqua regia, and the metal content in the solution was determined by ICP-AES. As it can be seen from Table 2, it is similar with the metal content in catalyst by calculated and determined. In other words, the metal additives were very easy to be loaded on the active carbon surface.

Long-term stability of trimetallic Au-Cu-La/AC catalyst

For the sake of economy and substantial industrial application, the long-term stability of trimetallic Au-Cu-La/AC with Au loading of 0.2 wt% was conducted. Using the acetylene hydrochlorination as the probe tests, the catalytic properties of Au-Cu-La/AC catalyst was prepared in a 100 L stainless autoclave, the weight fraction of Au, Cu and La in the sample was 0.2%, 2.5%, 2.35% respectively which was determined by ICP-AES.

The experiment results showed that the conversion of acetylene and the selectivity of VCM are all higher than 99% in 100 hours tests.

Although the Au-Cu-La/AC catalyst preparation which was lowered the content of noble Au, as for the conventional catalyst (HgCl_2/AC) for acetylene hydrochlorination, the cost is still quite high, so the lifetime of the catalyst is the critical to decide whether this mercury-free catalyst can be used in the industry. According to the reactor for the carbon-supported HgCl_2 as the catalyst, a multi-tubular fixed bed reactor comprising 202 tubes (diameter 38 mm \times 4000 mm), was designed and set up, the tubes were arranged by a regular triangle with the center distances between tubes of 60 mm. The loading catalyst volume in the reactor was 1 m³. The reactor was located in Tianjin Dagu Chemical Co., Ltd. Fig.4 shows the flow chart and appearance of the single-tube reactor for acetylene hydrochlorination.

In this work, the catalytic performance in acetylene hydrochlorination was carried out on a multi-tubular fixed bed reactor pilot unit, the reaction conditions have already been given in the catalytic tests. The feed materials of acetylene and hydrogen chloride are bypassed from the raw materials pipes for the industrial acetylene hydrochlorination progress based on mercuric chloride catalyst. The results of the 3,500-hour run (in Fig. 5) showed that the acetylene conversion rate remained stable over 98.5% with the fluctuations less than 1%, and the selectivity of vinyl chloride maintained a stability of 99% or higher, which indicated that the mercury free catalyst has excellent catalytic performances for acetylene hydrochlorination. Compared with the previous catalyst Au-Cu-K/AC, as shown in Fig. 6, the selectivity of the catalyst Au-Cu-La/AC for VCM is more stable and there is no sudden drop. Moreover, the conversion of ethylene is significantly improved and more stable than that of the catalyst Au-Cu-K/AC.

Table 2: The metal content of fresh Au-Cu-La/AC catalyst.

Catalysts	Au	Cu	La
Calculated	0.21%	2.50%	2.35%
Determined	0.20%	2.34%	2.42%

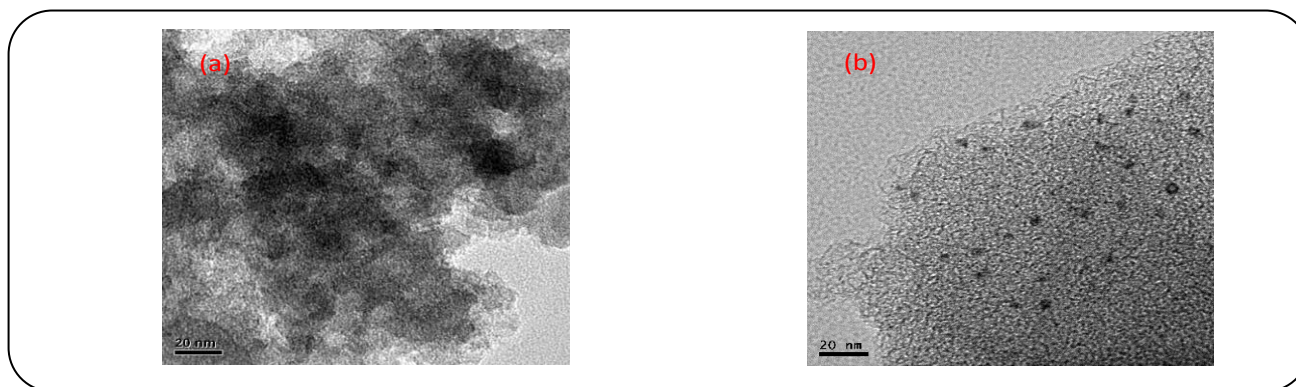


Fig. 3: The TEM images of catalysts: (a) fresh Au-Cu /AC; (b) fresh Au-Cu-La/AC.



Fig. 4: Pictures of the multi-tubular fixed bed reactor for acetylene hydrochlorination.

CONCLUSIONS

The metal chloride of LaCl_3 was chosen to modify the Au-Cu/AC to decrease the noble metal of gold and enhance the catalytic performances. Then a mercury-free catalyst of Au-Cu-La/AC was prepared by impregnation method. The additives of La with Cu can make the active species dispersed well and retard the aggregation of particles. The catalytic performances of mercury-free catalyst for acetylene hydrochlorination were carried out for 3500 hours in a multi-tubular fixed bed reactor pilot unit. The results showed that the acetylene conversion rate remained stable over 98.5%

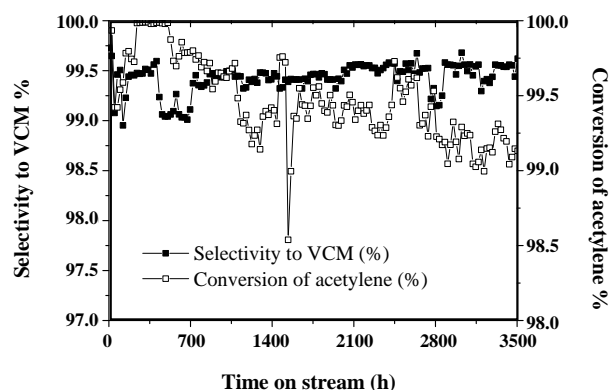


Fig. 5: The Catalytic performance of Au-Cu-La/AC catalyst.

with the fluctuations less than 1%, and the selectivity of vinyl chloride maintained a stability of 99% or higher, which indicated that the mercury free catalyst has excellent catalytic performances for acetylene hydrochlorination.

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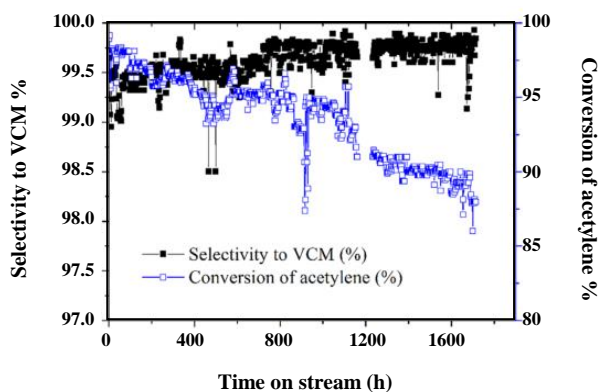


Fig. 6: The Catalytic performance of Au-Cu-K/AC catalyst.

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