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A novel high-stability Au (III)/Schiff-based catalyst for acetylene

hydrochlorination reaction

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Abstract Herein, we reported on the application of an Au (III)/Schiff-based catalyst in acetylene hydrochlorination reaction. The [AuCl₂(phen)]Cl catalyst exhibited excellent stability, and acetylene conversion was maintained at >90% after 40 h of operation. The excellent stability of the [AuCl₂(phen)]Cl catalyst was attributed to the presence of the 1,10-phenanthroline ligand that partially inhibited the reduction of the Au³⁺ active component.

Keywords: [AuCl₂(phen)]Cl; acetylene hydrochlorination

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1.Introduction

Acetylene hydrochlorination is an important industrial route to the manufacture of vinyl chloride monomer. However, the HgCl₂ catalyst used in acetylene hydrochlorination is highly toxic and causes serious environmental problems. Therefore, the use of non-mercury catalysts in acetylene hydrochlorination has been extensively explored.

Since 1975, K. Shinoda et al. discovered the catalytic activity correlates well with the standard electrode potential of the metal, and a supported Au-based catalyst with excellent catalytic performance in acetylene hydrochlorination reaction [1, 2]. However, Au-based catalysts rapidly deactivate during acetylene hydrochlorination as a result of the deactivation of active Au^{3+} to Au^{0} [3, 4]. Considerable efforts have been exerted to enhance the stability of AuCl₃ catlasyt by addition of another metallic component. Hutchings et al. investigated the effect of adding Ru^{3+} , Ir^{3+} , Pd^{2+} , Pt^{4+} and Rh³⁺ on the stability of Au³⁺ for acetylene hydrochlorination, and the results showed that these bimetallic ions provided no obviously improvement for inhibiting the Au³⁺ to Au⁰ [5]. Wang et al. reported that AuCl₃-CuCl₂/AC catalyst did not deactivate after running more than 200 h on the stream [6]. Zhang et al. also reported AuCl₃-Co(III)/SAC catalysts displays a fairly stable activity, with approximately 92% acetylene conversion and 99.9% selectivity to VCM. No visible decline in activity is observed [7]. Catalytic properties affected by the second metallic component are attributed to changes in the electronic structure of the active metal, due to electron-transfer between Au and another metal chloride. Our group found that the

property of carbon support can also affect the sability of AuCl₃ for acetylene hydrochlorination. With N-doped carbon nanotubes (CNT) as support, AuCl₃ displaysed enhanced stbaility for acetylene hydrochlorination compared with that with CNT as support, attributed to electron transfer between the N atom Au³⁺ active site [8].

Previous literature reported that a gold/Schiff-based complex has a higher positive-redox potential than the AuCl₃ compound [9], indicating that the presence of N-containing ligands that could inhibit the reduction of Au^{3+} to Au^0 [10, 11]. Therefore, it can be inferred that the presence of N-containing component as ligands may enhance the stability of AuCl₃ catalyst for acetylene hydrochlorination. In this paper, we will try to synthesize a gold/Schiff-based complex and apply it in acetylene hydrochlorination. The synthesized catalyst was characterized by a series of characterization to determine its physical property, and its catalytic performance was evaluated by a fixed-bed reactor.

2. Experimental

2.1. Materials

Activated carbon (marked as AC, neutral, 20-40 mesh); HAuCl₄·4H₂O (the content of Au assay 47.8%); 1, 10-phenanthroline; C₂H₂ (gas, 98%); HCl (gas, 99%).

2.2. Catalyst synthesis and preparation

2.2.1. Catalyst synthesis

In the general catalyst synthesis, an ethanol solution of 1,10-phenanthroline (10 mL, 0.96 M) was added to an ethanol solution of 1.0 g HAuCl₄ (10 mL) under

stirring. The mixture was stirred for 4 h under reflux conditions. At the end of the reaction, a large amount of yellow or orange solid was formed. After filtration, washing with ethanol (3×5mL), and drying in air, [AuCl₂(phen)]Cl (**1Au**) was obtained. Anal. Found: UV-Vis: λ_{max} (CH₃OH)/nm (Fig. S1): 230, 280, 317; IR (KBr, cm⁻¹): 1630, 1590, 1512, 1486, 1414, 1205, 866, 703 cm⁻¹ (Fig. S2); and ¹HNMR (DMSO-d₆, δ , ppm): 9.31 (d, 2H), 9.05 (d, 2H); 8.35 (s, 2H) 8.22(m, 2H); ¹³CNMR (DMSO): 147.60, 141.74, 137.51, 129.47, 127.44, 125.61 (Fig. S3).

2.2.2 Catalysts preparation

2.2.2.1 AuCl₃/AC

The supported gold catalyst AuCl₃/AC was prepared using an impregnation technique with hydrochloric acid as a solvent. 3.2 mL (solution, 1 g/100 mL) HAuCl₄·4H₂O was added dropwise to 3.0 g activated carbon under stirring for 12 h, and then dried at 140 °C for 18 h. AuCl₃/AC catalyst was prepared. The actual loading of gold was 0.49 wt.% determined by an inductively coupled plasma.

2.2.2.2 1Au/AC

The supported gold catalyst **1Au** was prepared using an impregnation technique with hydrochloric acid as a solvent. Then 0.0375 g **1Au** was dissolved in 9 mL hydrochloric acid, and then added dropwise to 3.0 g activated carbon under stirring for 12 h. Finally, **1Au**/AC catalyst was dried at 140 °C for 18 h. The actual loading of gold was 0.49 wt.% determined by an inductively coupled plasma.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) experiment used a JEM-2010 electron

microscope with the accelerating voltage of 200 kV, a line resolution of 0.14 nm and point-to-point resolution of 0.23 nm. The X-ray diffraction (XRD) data was collected on a Bruker advanced D8 X-ray diffractometer using Cu-K α irradiation ($\lambda = 1.5406$ Å) as source at 40 kV and 40 mA in the scanning range of 20 between 10° and 90°. X-ray photoelectron spectroscopy (XPS) data was recorded on a Thermo ESCALAB 250XI experiment, using a monochromatised Al, Ka X-ray source (225 W), minimum energy resolution 0.45 eV (Ag 3d_{5/2}) and the minimum XPS analysis area 3 um.

2.4. Catalytic performance evaluation

Activity test was carried out in a fixed bed reactor. Before the reaction, the reactor was purged with nitrogen to remove water and air in the reacting system. Hydrogen chloride gas was passed through the reactor with the flow rate of 20 mL/min to activate the catalyst. After the reactor was heated to 180 °C, acetylene (9.3 mL/min) and hydrogen chloride (11.2 mL/min) were fed through the heated reactor containing 2 mL of catalyst, giving a gas hourly space velocity (GHSV) of 603 h⁻¹. The exit gas mixture was passed through a Dreschel bottle containing water to remove hydrogen chloride. Compositions of the product were analyzed with GC-2014C gas chromatograph produced by Shimadzu international trading Ltd Company (Shanghai). The conversion of acetylene (X_A) and the selectivity to VCM (S_{VC}) as the criteria of catalytic performance were defined as following equations, respectively.

$$X_{A} = \frac{\Phi_{A0} - \Phi_{A}}{\Phi_{A0}} \times 100\%$$
(1)

$$S_{VC} = \frac{\Phi_{VC}}{1 - \Phi_A} \times 100\%$$
⁽²⁾

In the above equations, Φ_{A0} was defined as the volume fraction of acetylene in the raw gas, and Φ_A was defined as the volume fraction of remaining acetylene in the product gas. Φ_{VC} was the volume fraction of vinyl chloride in product gas.

3. Results and discussions

Fig. 1 displays the redox potentials of the **1Au** and AuCl₃ catalysts. The peaks at 0 and -0.7 V in AuCl₃ catalyst were attributed to the reduction of Au³⁺ to Au⁺ and Au⁺ to Au⁰, respectively. A positive shift in both reduction peaks was evidently observed in the **1Au** catalyst. Hence, the Au³⁺ oxidation state in the complex **1Au** was confirmed by electrochemistry. At the same time, this result also suggested that the introduction of the phen ligand may inhibit the reduction of Au³⁺ to metallic Au⁰, which is consistent with the findings in previous literature [10, 11].

The thermal stability of the synthesised **1Au** catalyst was investigated to confirm whether the decomposition of the ligand occurred under reaction temperature of 180 °C. The thermogravimetric analysis (TGA) of the **1Au** catalyst was shown in Fig. S4. The results show that the decomposition temperature of the **1Au** catalyst is 270 °C, thus indicating that the catalyst is stable under the reaction condition of acetylene hydrochlorination.

The catalytic performances of the AuCl₃/AC and **1Au**/AC catalysts were tested under the same conditions (temperature (T) = 180 °C, C_2H_2 gas hourly space velocity (GHSV) = 280 h⁻¹, feed volume ratio V_{HCl}/V_{C2H2} = 1.2). In order to demonstrate the effect of HCl pretreatment on AuCl₃/AC catalyst, we compared the catalytic performance of AuCl₃/AC for acetylene hydrochlorination, and characterized the used

AuCl₃/AC catalysts with and without the presence of HCl pre-treatment. The results are shown in Fig. S5, Fig. S6 and Fig. S7 in the Supporting Information. It can be inferred that HCl pre-treatment can partly inhibit the reduction of Au³⁺ active component, and thus improve the catalytic activity of AuCl₃/AC catalyst. Acetylene conversion and VCM selectivity are shown in Fig. 2. The two catalysts exhibit relatively similar initial catalytic activities and selectivity, with almost 96% acetylene conversion and 99.5% selectivity. However, AuCl₃/AC acetylene conversion decreased from 96% to 69% after 40 h of operation, thus demonstrating the deactivation of the AuCl₃/AC catalyst. In addition, the 1Au/AC catalyst exhibited good stability in the acetylene hydrochlorination process, and over 90% of the converted acetylene was maintained after 40 h of operation. This result indicated that the **1Au**/AC catalyst displayed a slower deactivation rate than the AuCl₃/AC catalyst in acetylene hydrochlorination. Therefore, both electrochemistry investigation and catalytic test using AuCl₃ and **1Au** demonstrate undoubtedly that the enhancing effect of the nitrogen-containing ligand 1, 10-phenanthroline on the stability of Au(III) is the key to render Au(III) species efficient for hydrochlorination catalytic reaction.

The activity of Au-based catalysts for hydrochlorination reaction of acetylene decreases along the order: $Au^{3+} > Au^+ > Au^0$, therefore, the reduction of Au^{3+} to metallic Au^0 is the predominant reason for the rapid deactivation of $AuCl_3/AC$ catalyst, as shown in Fig. 2. In addition, the higher positive-redox potential can inhibit the Au^{3+} to Au^0 . In order to provide evidence for this viewpoint, we carried out XRD to demosntrate the state of Au in the fresh and used AuCl₃ and **1Au** catalysts. From

Fig. 3, it is obviously that the fresh Au-based catalysts have no peaks of metallic Au^0 , however, the used Au-based catalysts display diffraction peaks of Au^0 at 38.5^0 , 44.7^0 and 64.8^0 , which is well matched with the standard data of metallic Au^0 (PDF # 04-0784). The result also shows that sintering exists in Au-based catalysts to some extent after the reaction. It is important to note that the addition of additives can't inhibit the sintering of the Au catalyst in the reaction process, but can retard the reduction of the active component to a certain extent.

Fig. 4 shows TEM images of the fresh and used AuCl₃/AC (Fig. 4a and Fig.4c) and **1Au**/AC (Fig. 4b and Fig.4d) catalysts after 40 h reaction. From Fig. 5, it can be seen that there is no obviously nano-Au particles in fresh Au-based catalysts, however, the coverage density of nanoparticles are obviously increased after reaction. In addition, for the used **1Au**/AC catalyst experiencing reaction, the Au naono-partiles are much more sparsely than used AuCl₃/AC catalyst, being consitent with XRD results. The average particle size of the used AuCl₃/AC and **1Au**/AC catalyst is 24 nm and 23 nm, from Fig. 4c and Fig. 4d. That results are somewhat larger than calculted from Scherrer equation, which is 14.7 nm and 13.2 nm. This phenomenon may be attributed that the crystalline size of nano-particle is smaller than its actual size.

The XPS spectra of the fresh and used Au-based catalysts corresponding to Au 4f peaks are shown in Fig. 5 All of the Au (4f) signals have been deconvoluted into three components responding to metallic Au and oxidized Au species. Calculated from the relative deconvoluted peak area, the ratios of metal oxide species in the catalysts are listed in Table 1. According to these data, the content of Au^{3+} is 44% presented in

fresh AuCl₃/AC catalyst, and the content of Au³⁺ is 40% also observed in **1Au**/AC catalyst. However, the content of Au³⁺ in used AuCl₃/AC and **1Au**/AC catalyst is 20% and 35%, respectively. The higher content of Au³⁺ in used **1Au**/AC catalyst may be attributed that N-containing ligands inhibited the reduction of Au³⁺ to Au⁰ comparing with AuCl₃/AC catalyst, which is consistent with Fig. 1 and Fig. 3. In addition, it is noted that the binding energy of Au 4f_{7/2} of fresh **1Au**/AC catalyst shows a significant negative shift (about 0.1 eV) comparing with fresh AuCl₃/AC catalyst. Such a negative shift has been ascribed to the interaction between Au and phen, which increases the electron density of Au³⁺ with the transfer of electron from phen species to Au³⁺ centre, and thus inhibit the reduction of active Au³⁺ component.

4. Conclusions

In summary, the synthesised 1Au/AC catalyst exhibited excellent stability in acetylene hydrochlorination reaction. The enhanced catalytic stability was attributed to the presence of the phen ligand, which inhibited active Au^{3+} component deactivation. The 1Au/AC catalyst may be a candidate catalyst in industrial application of acetylene hydrochlorination due to its excellent performance.

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Figure Captions:

Fig. 1 Linear potential-scan voltammograms of (A) HAuCl₄ and (B) **1Au** complex in acetonitrile solution in an argon atmosphere.

Fig. 2 (A) conversion of acetylene and (B) selectivity to VCM in acetylene hydrochlorination over (a) AuCl₃/AC and (b) **1Au**/AC catalysts. Reaction conditions: temperature (T) = $180 \,{}^{0}$ C, C₂H₂ GHSV = $280 \,{}^{h-1}$, feed volume ratio V_{HCl}/V_{C2H2} = 1.2. **Fig. 3** XRD patterns of (a) AC, (b) fresh AuCl₃/AC, (c) fresh **1Au**/AC, (d) used AuCl₃/AC and (e) used **1Au**/AC catalysts.

Fig. 4 TEM images of fresh and used Au-based catalysts. (a) fresh AuCl₃/AC; (b) fresh **1Au**/AC; (c) used AuCl₃/AC and (d) used **1Au**/AC catalysts.

Fig. 5 (A) high-resolution XPS spectra for Au 4f of (a) fresh AuCl₃/AC and (b) used AuCl₃/AC catalysts; (B) high-resolution XPS spectra for Au 4f of (a) fresh **1Au**/AC and (b) used **1Au**/AC catalysts

Table 1 The binding energies and relative intensities as observed from the Au (4f)

Catalysts	Relative of intensity (%)		
	Au ⁰ 4f	Au ⁺ 4f	$Au^{3+} 4f$
fresh AuCl ₃ /AC	49	7	44
used AuCl ₃ /AC	65	15	20
fresh 1Au /AC	49	2 11	40
used 1Au /AC	55	10	35

spectrum of AuCl_3/AC and 1Au/AC catalysts



Fig. 1 Linear potential-scan voltammograms of (A) HAuCl₄ and (B) **1Au** complex in acetonitrile solution in an argon atmosphere.



Fig. 2 (A) conversion of acetylene and (B) selectivity to VCM in acetylene hydrochlorination over (a) AuCl₃/AC and (b) **1Au**/AC catalysts. Reaction conditions: temperature (T) = $180 \ {}^{0}$ C, C₂H₂ GHSV = $280 \ {}^{-1}$, feed volume ratio V_{HCl}/V_{C2H2} = 1.2.



Fig. 3 XRD patterns of (a) AC, (b) fresh AuCl₃/AC, (c) fresh 1Au/AC, (d) used

AuCl₃/AC and (e) used **1Au**/AC catalysts.



Fig. 4 TEM images of (a) fresh AuCl₃/AC; (b) fresh 1Au/AC; (c) used AuCl₃/AC and

(d) used **1Au**/AC catalysts.



Fig. 5 (A) high-resolution XPS spectra for Au 4f of (a) fresh AuCl₃/AC and (b) used AuCl₃/AC catalysts; (B) high-resolution XPS spectra for Au 4f of (a) fresh **1Au**/AC and (b) used **1Au**/AC catalysts

Highlights:

► [AuCl₂(phen)]Cl catalyst is synthesized and applied in acetylene hydrochlorination.

► [AuCl₂(phen)]Cl catalyst displays excellent stability for acetylene hydrochlorination.

• N-containing ligands inhibit the reduction of active Au^{3+} component.

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