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Mercury-Free Catalyst Preparation for Acetylene Hydrochlorination and it's Catalytic Performance on Single-Tube Pilot Unit Compared with $HgCl_2$ Catalyst

LEI WANG[1,2], BENXIAN SHEN[1], RUOFAN REN[1,2], WEIGUO XIAO[2] and JIGANG ZHAO[1,*]

[1]State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P.R. China
[2]Tianjin Dagu Chemical Co. Ltd., Tianjin 300455, P.R. China

*Corresponding author: Fax: +86 21 64252851; Tel: +86 21 64252916; E-mail: zjg@ecust.edu.cn

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The mercury-free catalyst of Au-Cu-K/AC was prepared in a 10 L autoclave and characterized by ICP-AES, BET, SEM and TEM. The comparison test for hydrochlorination of acetylene with an industrial $HgCl_2$ catalyst was conducted in a single-tube pilot unit with paralleled reactors under the same experimental conditions. The characterization results show that the mercury-free catalyst of Au-Cu-K/AC has a micropore structure, the particle size of the active component of 4 nm and loaded components enhance in HCl adsorption and desorption temperature. The catalytic tests indicate that the vinyl chloride monomer selectivity of mercury-free catalyst for Au-Cu-K/AC is more than 99 % which equal to that of the industrial $HgCl_2$ catalyst. The C_2H_2 conversion of industrial $HgCl_2$ catalyst is more than 98 % in the first 900 h, but declines in the following 700 h; while the conversion of C_2H_2 by mercury-free catalyst reduced slowly from 98 to 89 % in the whole 1600 h on stream, thus the mercury-free catalyst has a better stability.

Keywords: Mercury-free catalyst, Acetylene hydrochlorination, Single-tube pilot.

INTRODUCTION

Vinyl chloride monomer (VCM) is mainly used for synthesis of polyvinyl chloride (PVC) which is widely used in every aspect of life. As the world's largest PVC producing country, China has over 12.5 Mt/a PVC synthesized from the calcium carbide method and this route dominates about 81 % of the gross PVC production in China[1,2]. It is based on the catalyst of $HgCl_2$ supported on the activity carbon[3,4]. However, the toxicity and volatility of the $HgCl_2$ cause serious troubles in environment and health to human beings encouraging us to search for mercury-free catalytic systems. Facing the harmful pollution of $HgCl_2$, the development of novel Hg-free catalysts is extremely urgent for establishing a sustainable PVC industry in China[5,6].

Recently, there have been many studies dealing with the hydrochlorination of acetylene using supported gold as catalysts[7-11]. One advantages of using this metal are its higher activity, compared with the mercuric-based catalysts, allowing the use for industrial application[7]. Although gold can be considered as the best catalyst in terms of initial activity, severe deactivation is still the main problem of the supported gold catalyst system employed for selective hydrochlorination of acetylene. Conte *et al.*[10] reported that Au catalyst lost about 10 % of its initial activity within 2 h of the reaction. High costs and difficulty of purification together have largely limited the application and development of gold-based catalysts in industrial hydrochlorination of acetylene[12,13]. Alloying Au with other base metal was a promising way to improve the catalytic activity and a bimetallic Au-Cu/AC catalyst showed promising catalytic activity and an acetylene conversion of 99.5 % at 200 h[6]. However, the industrial scale-up of mercury-free catalyst for future PVC processes was less reported, thus, the industrial scale-up needs further research.

In present work, the mercury-free catalyst was prepared by 10 L autoclave and was characterized by BET, TEM and HCl-TPD and the catalytic performance was firstly carried out in the lab unit. Furthermore, the comparison test for hydrochlorination of acetylene with an industrial $HgCl_2$ catalyst was conducted in a single-tube pilot unit with paralleled reactors under the same experimental conditions for 1600 h.

EXPERIMENTAL

Acetylene (99.5 %) and hydrogen chloride (99 %) were all from Tianjin Dagu Chemical Co., Ltd. Activated carbon (AC8-12 mesh, coconut shell) is from Shanghai Xinhui activated carbon Co., Ltd. A HAuCl4·4H2O (assay: 49.7 %) solution is from sinopharm chemical reagent Co., Ltd.

General procedure: Au-Cu-K mercury-free catalyst was prepared in 10 L stainless autoclave using a wetness

impregnation technique. Activated carbon (AC) (8-12 mesh) was washed with dilute aqueous HNO_3 to eliminate impurities, which are poisons for the hydrochlorination reaction. Certain amounts of $HAuCl_4 \cdot 4H_2O$ (content of Au assay 49.7 %), $CuCl_2 \cdot 2H_2O$ and KCl were dissolved in deionized water to make a solution impregnation, activated carbon were added to certain concentration amount of a mixed solution of $CuCl_2$, $HAuCl_4$ and KCl, impregnated for 5 h and then dry at 110 °C, to prepared mercy-free catalyst, For convenience, the catalyst denoted Au-Cu-K/AC succinctly.

Detection method: The catalytic performance in hydrochlorination of acetylene was evaluated in a fixed-bed microreactor (diameter 10 mm) under the pressure of 0.1 MPa and temperature of 165 °C. To begin with the reactor was purged with nitrogen to remove water in the reaction system. Hydrogen chloride 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 150 °C, acetylene (20 mL/min) and hydrogen chloride (22 mL/min) were fed through the heated reactor which loaded 10 mL catalyst.

The catalytic performance compared with $HgCl_2$ catalyst was conducted in a fixed-bed reactor (diameter 40 × 4000 mm) by a single-tube pilot unit, which was located in Tianjin Dagu Chemical Co., Ltd. The flow charts was shown in Fig. 1. The reactor was purged with nitrogen to remove water in the reaction system before the reaction process. Hydrogen chloride passed through the reactor at a flow rate of 1 L/min for 2 h to activate the catalyst. After the reactor was heated to 165 °C, acetylene and hydrogen chloride were fed through the heated reactor which contained catalyst. The GSHV based on total feed was controlled at 40 h^{-1} and the mole ratio of HCl to C_2H_2 was 1.05.

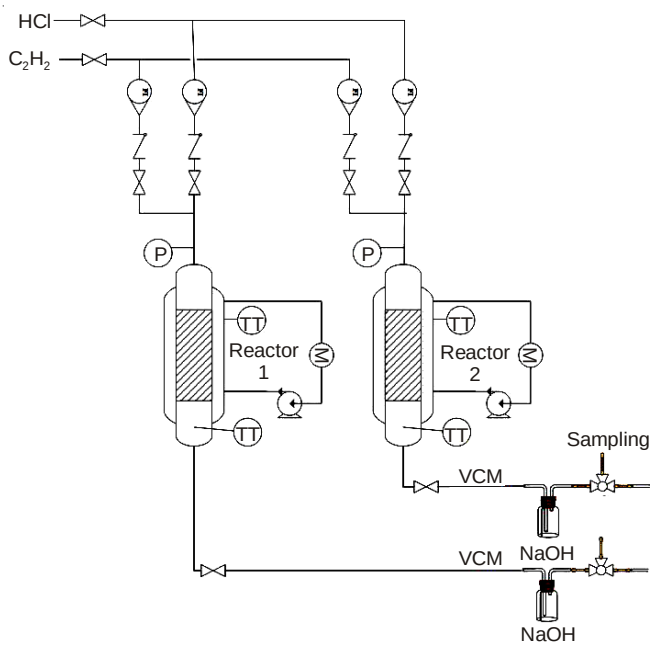

Fig. 1. Schematic diagram of hydrochlorination of acetylene reaction in single-tube pilot experiment

The reaction product was analyzed by gas chromatography (GC-920, Al_2O_3 PLOT column). The catalyst activity is determined by the conversion of acetylene ($X_{C_2H_2}$) and selectivity of VCM (S_{VCM}), which are defined as:

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

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

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

The surface area and pore size distribution was measured through nitrogen physico-sorption using a Micromeritics ASAP2020 automatic system. The samples were previously degassed at 300 °C under high vacuum. Surface areas of different materials were calculated by using the BET equation. The pore size distribution was obtained applying the Barret-Joyner-Halenda (BJH) model with the cylindrical pore geometry.

Temperature programmed analysis (including HCl-TPD) was carried out in a Micromeritic ASAP 2920 equipped with a thermal conductivity detector (TCD). The sample was placed into a quartz tube and degassed in a He flow (50 mL/min) at 250 °C, with the temperature being kept constant for 15 min. Then, the sample was cooled down to 50 °C. The gas mixture containing 10 % NH_3 balanced with argon (or pure HCl gas, flow rates of 50 mL/min) was passed over the samples for 60 min as an adsorption gas. After being purged with pure He for 90 min at the same temperature, a temperature ramp from 50 to 600 °C (ramp rate, 10 °C/min) for desorption under helium flow (30 mL min^{-1}).

TEM experiments used a JEM-2100F electron microscope with the accelerating voltage of 200 kV, a line resolution of 0.14nm and point-to-point resolution of 0.23 nm.

Metal content analysis using Varian's 710ES inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement instrument. Plasma gas flow rate of 15 mL/min, atomizing air pressure 200 kPa.

RESULTS AND DISCUSSION

Properties of Au-Cu-K/AC: Table-1 listed the textural properties of activated carbon and Au-Cu-K/AC. It indicated that activated carbon had a micro porous structure, with a specific area (SSA) of above 1038 m^2/g. After loading the active component of Au, Cu and K, the specific area of ACH decreased slightly from 1038 m^2/g to 1008 m^2/g, due to the active species filling or blocking part of the pores.

TABLE-1
TEXTURAL PROPERTIES OF SAMPLES

Samples	SSA ($m^2\ g^{-1}$)	V ($cm^3\ g^{-1}$)	Mean pore size (nm)
Activated carbon	1038	0.415	2.07
Au-Cu-K/AC	1008	0.382	1.89

SSA: BET surface area; V: total pore volume;
D: average pore diameter

Compositions of Au-Cu-K nanoparticles were characterized by transmission electron microscopy (TEM) and the image was presented in Fig. 2. The darker spots in the image represented the loaded component particles with the mean diameter of 4 nm, which was given in Fig. 3. The results indicated that the loaded particles were uniformly dispersed and not agglomerated on the surface of the activated carbon support.

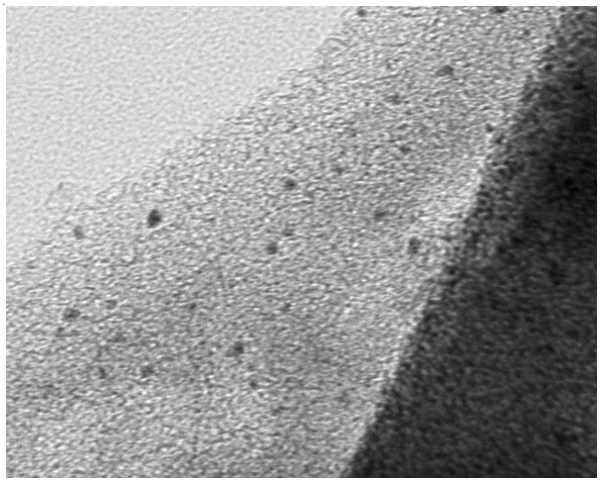

Fig. 2. TEM image of Au-Cu-K/AC

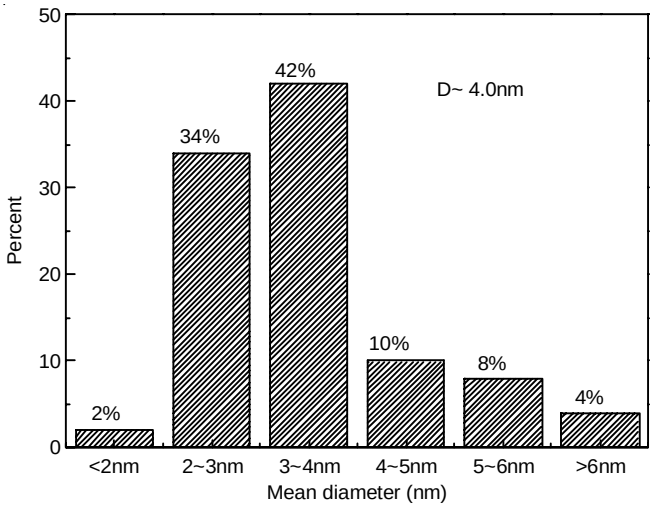

Fig. 3. Particle size distribution of Au-Cu-K/AC

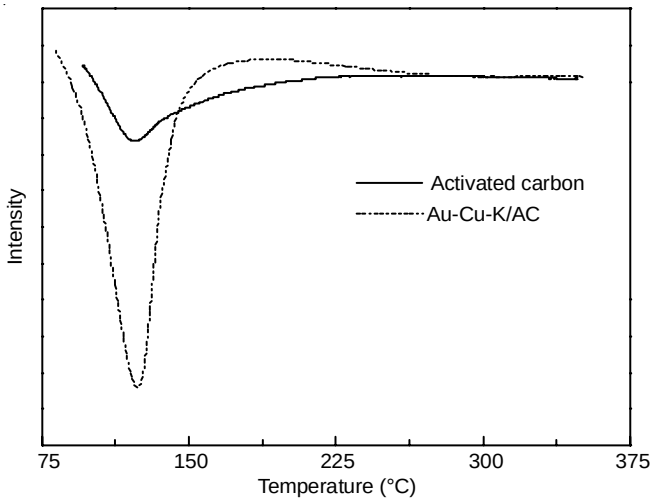

Fig. 4. Hydrogen chloride TPD profiles of activated carbon and Au-Cu-K/AC

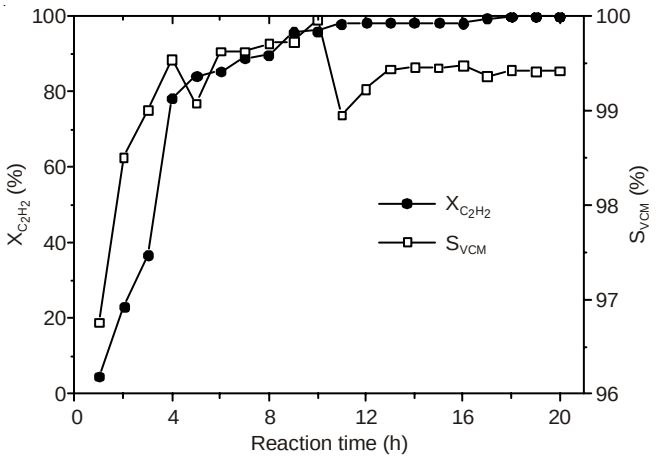

Fig. 5. Catalytic activity of Au-Cu-K/AC

Hydrogen chloride TPD profiles for activated carbon and Au-Cu-K/AC were presented in Fig. 4. The desorption temperature in the TPD profiles reflects the binding strength of the adsorbed species on the catalyst surface and the peak area correlates with the amount of adsorbed species. As shown in Fig. 4, areas for Au-Cu-K/AC were significantly larger than activated carbon. Additionally, hydrogen chloride desorption temperatures increased as followed: AC < Au-Cu-K/AC, noting that Au-Cu-K/AC showed better ability of HCl adsorption than activated carbon. Therefore, the loaded components of Au, Cu and K had an enhancement in HCl adsorption and desorption temperature.

Catalytic activity: Using the hydrochlorination of acetylene as the probe tests, the catalytic properties of Au-Cu-K/AC catalyst was prepared in a 10 L stainless autoclave, the weight fraction of Au, Cu and K in the sample was 1.17 %, 3.27 %, 2.15 % respectively which was determined by ICP-AES. The prepared catalyst was loaded in the experimental unit and the reaction conditions were given in the experimental section. Catalytic activity results of Au-Cu-K/AC were given in Fig. 5. The results showed that the conversion of acetylene and the selectivity of VCM are all higher than 99 % in 20 h tests, which mean the catalyst showed a good performance in hydrochlorination of acetylene.

Long run test of Au-Cu-K/AC compared with $HgCl_2$ catalyst: Although a Au-Cu-K/AC catalyst preparation which was lowered the content of noble Au (1.17 wt %), as for the conventional catalyst ($HgCl_2$/AC) for acetylene hydrochlorination, the cost of mercury-free catalyst 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. So the long run test must need to be further investigated.

In this work, the catalytic performances of mercury-free catalyst compared with conventional catalyst ($HgCl_2$/AC) in hydrochlorination of acetylene were carried out on a single-tube pilot unit with 4 single-tube reactor. The reaction conditions have previously been given in the catalytic tests. 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 acetylene conversion and VCM selectivity of Au-Cu-K/AC and $HgCl_2$/AC catalyst were shown in Figs. 6 and 7, respectively. It can be seen that either of Au-Cu-K/AC and $HgCl_2$/AC catalyst have an excellent VCM selectivity, which was higher than 99 % during 1600 h on stream as showed in Fig. 7. And the acetylene conversions of Au-Cu-K/AC and $HgCl_2$/AC catalyst showed a different behaviour in Fig. 6, acetylene conversion of Au-Cu-K/AC catalyst is slowly lowered from

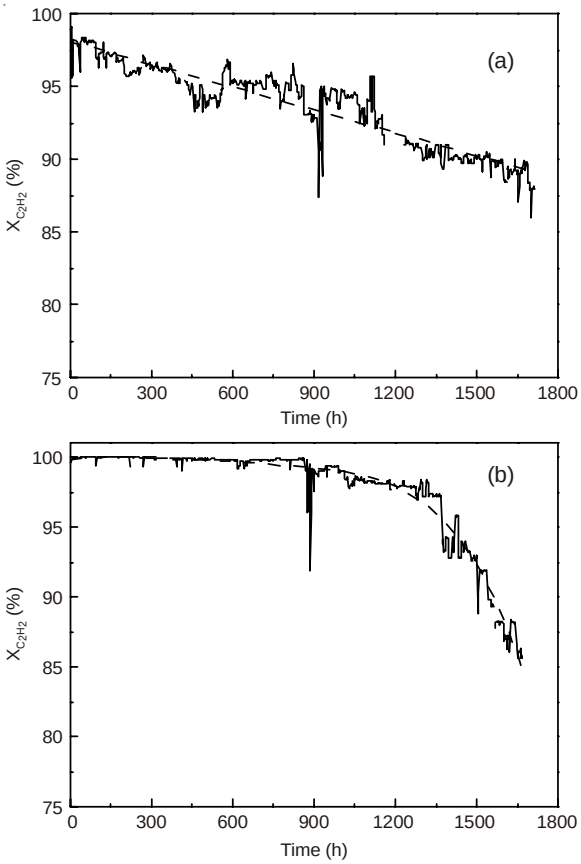

Fig. 6. C_2H_2 conversion *versus* reaction time of (a) Au-Cu-K/AC and (b) $HgCl_2$

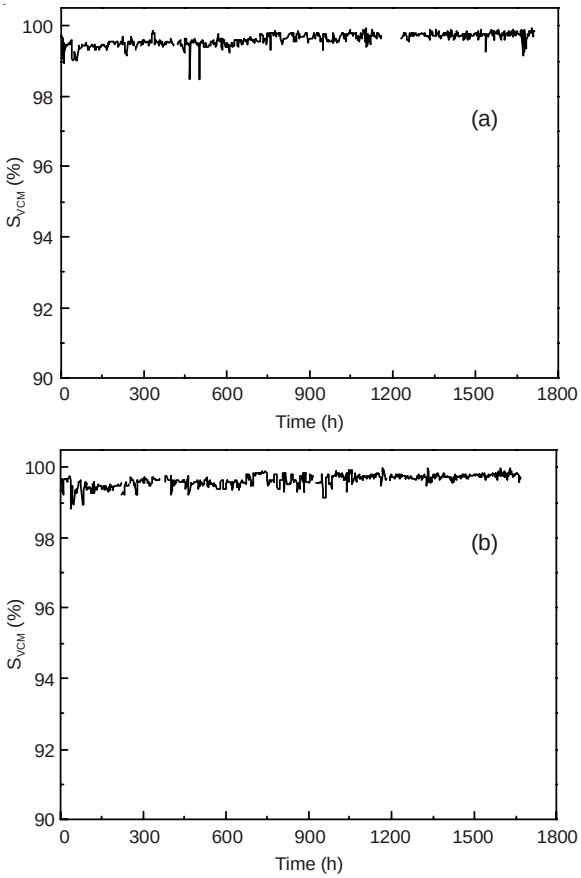

Fig. 7. VCM selectivity *versus* reaction time of (a) Au-Cu-K/AC and (b) $HgCl_2$

97 to 89 % during 1600 h on stream, while the $HgCl_2$/AC catalyst kept very stable during the first run of 900 h, after the reaction time of 1200 h, the acetylene conversion was decreased dramatically lowered from 97 to 85 %. It means that the catalyst of Au-Cu-K/AC has a better stability in acetylene hydrochlorination.

Conclusions

The mercury-free catalyst of Au-Cu-K/AC was successfully prepared in 10L autoclave and characterized by BET, TEM and HCl-TPD. The results showed that the Au-Cu-K/AC catalyst has a micro porous structure and the nanoparticles of mean diameter of 4 nm on the surface of activated carbon support and the loaded components of Au, Cu and K had an enhancement in HCl adsorption and desorption temperature. Meanwhile, catalytic performances in experimental unit showed that the conversion of acetylene and the selectivity of VCM are all higher than 99 % in 20 h tests.

Furthermore, the catalytic performances of mercury-free catalyst (Au-Cu-K/AC) compared with conventional catalyst ($HgCl_2$/AC) in hydrochlorination of acetylene were carried out on a single-tube pilot unit with paralleled reactors. The catalytic tests indicate that the VCM selectivity of mercury-free catalyst for Au-Cu-K/AC is more than 99 % which is equal to that of the industrial $HgCl_2$ catalyst. The C_2H_2 conversion of industrial $HgCl_2$ catalyst is more than 98 % in the first 900 h, but declines in the following 700 h; while the C_2H_2 conversion of mercury-free catalyst reduced slowly from 98 to 89 % in the whole 1600 h on stream, thus the mercury-free catalyst has a better stability.

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