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Non-mercury catalytic acetylene hydrochlorination over bimetallic Au-Ba(II)/AC catalysts

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Bimetallic gold-barium catalysts were prepared and assessed for acetylene hydrochlorination, combining with characterizations of low-temperature N_2 adsorption/desorption, thermogravimetric analysis, X-ray diffraction, temperature-programmed reduction/desorption, inductively coupled plasma-atomic emission spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The best catalytic performance is obtained over Au1Ba(II)1/AC catalysts with the acetylene conversion of 98.4% and the selectivity to VCM of 99.9%. It is indicated that the addition of Ba(II) can make Au species dispersed well and inhibit carbon deposition on the catalyst surface; Ba(II) additives can enhance the adsorption of reactants on the catalysts but also inhibit the reduction of active gold species during the reaction, consequently augmenting the activity and long-term stability of gold catalysts.

1. Introduction

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Vinyl chloride monomer (VCM), which was mainly used to synthesize polyvinyl chloride (PVC), was first produced commercially by acetylene hydrochlorination over mercuric chloride catalysts in the 1930's. As ethylene became plentiful in the early 1950's it quickly displaced acetylene as the major feedstock, thus, direct chlorination and oxychlorination of ethylene become the principal processes gradually employed commercially for acetylene hydrochlorination.[1] Since 1980's acetylene hydrochlorination has received considerable attention again, especially in countries with large coal reserves, due to the serious economic challenges because of the increasing cost of ethylene resulting from the oil crisis.[2] However, the mercuric chloride catalysts has become a constraining bottleneck for the sustainable production of VCM via acetylene hydrochlorination reaction, owing to the highly toxic and volatile mercuric chloride causing serious damages to the workers and the environment.[1, 3-6] Therefore, studies of non-mercury catalyst to replace the mercuric chloride catalyst are extremely important for the survival and development of PVC industry.[7-33]

In the early years, a number of workers conducted some comparative studies on the hydrochlorination of acetylene using a range of metal chlorides supported on carbon or silica,[7, 8, 34-36] and found that the conversion of acetylene increased in the order: Pd(II) > Hg(II) > Cu(II) ~ Cu(I) > Ag(I) > Cd(II) > Zn(II); carbon was considered to be the superior support[36] and when silica was utilized some polymerization products were observed due primarily to surface acidity.[7] Hutchings group[9-17, 37-41] conducted the most valuable researches in acetylene hydrochlorination. In 1975, Shinoda[8] used over 20 types of metal components for acetylene hydrochlorination. Whereafter, Hutchings[9] analyzed the results and found that the catalytic activity was correlated with the standard electrode potential of the cations. The order of initial activity was consistent with the results in the early studies.[7, 8, 34-36] Afterwards, the researchers in Hutchings group studied the catalytic performance of activated carbon-supported gold (Au/C) catalysts in detail and concluded that Au was highly active for acetylene hydrochlorination, in fact, the initial activity of Au catalysts was higher than that of other metal catalysts, including $HgCl_2$ catalysts.[12-15] However, the activity and stability of monometallic Au/C catalyst is still poor in the long-time running. A potential method by which to improve catalytic activity is incorporation of other metals into the Au catalyst. Conte et al.[14] studied Au-M (M = Pd, Pt, Ir, Rh, and Ru) catalysts and found that addition of Pd to Au catalyst increased the initial activity of the resultant catalyst but greatly decreased the selectivity. Au-Pd/C and Pt-Au/C catalysts were also deactivated rapidly by coke deposition. Au catalysts doped with Ir and Rh demonstrated high activity with no obvious change in selectivity, whereas addition of Ru to the Au catalyst induced no significant effects. Shen et al.[19] reported that addition of Cu to Au catalyst (Au1Cu5/C, w/w; total metal amount of 3 wt%) promoted 100% acetylene conversion and featured stability exceeding 200 h under optimized conditions [temperature, 160 ℃; $V_{HCl}/V_{C_2H_2}$, 1.15; total gas hourly space velocity (GHSV), 50 h^{-1}]. Wei et al.[42] incorporated Bi(III) to Au catalyst and found that the addition of Bi(III) inhibited the reduction of Au and retained the active species in the form of Au^+ in the catalyst preparation and reaction process, resulting in

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the improvement of the catalytic activity. We also reported in the previous literatures that La(III) and Co(III) components in Au-based catalysts inhibited carbon deposition and the reduction of gold to improve the stability of the resultant catalysts.[24, 43] Under reaction conditions [temperature, 150 ℃; $V_{HCl}/V_{C_2H_2}$, 1.15; GHSV(C_2H_2), 360 h^{-1}], spherical activated carbon-supported Au1M3 [a/a, Au amount of 1 wt%, and M = La(III), Co(III)] catalysts can give a 100% initial acetylene conversion; however, conversion losses of 11% and 7% for Au-La(III) and Au-Co(III) catalyst respectively after 48 h of reaction had been observed. Despite all these encouraging findings, augmenting the long-term stability of Au-based catalysts for acetylene hydrochlorination is still a research focus.

Ba(II) was widely used as a promoter in Au-Ba(II)/Ti-TUD[44] and trimethylsilylated Ba(II)-Au/titanosilicate (Ti/Si 3:100) catalysts[45, 46] for propylene epoxidation. The addition of Ba(II) greatly increased propylene conversion respectively by 55.6% for Au-Ba(II)/Ti-TUD (temperature = 150 ℃; pressure = 0.1 MPa; space velocity = 7000 $cm^3\ h^{-1}\ g^{-1}_{cat}$; pH = 9.0) and by 48.5% for Ba(II)-Au/titanosilicate (temperature = 160 ℃; pressure = 0.1 MPa; space velocity = 4000 $cm^3\ h^{-1}\ g^{-1}_{cat}$; pH = 7.0) catalysts. Ba(II) also acted as a promoter of mercury chloride catalysts for the electronic effect due to its ionic nature in acetylene hydrochlorination reaction.[9, 47] We are enlightened to consider whether or not the addition of Ba(II) could improve the performance of Au catalysts for acetylene hydrochlorination. In this work, aiming to develop an efficient non-mercury catalyst, herein we investigated the effect of Ba(II) additive on Au-based catalysts for acetylene hydrochlorination. Several bimetallic gold-based catalysts were prepared on coconut shell activated carbon (AC), and the effects of the metal additive Ba(II) on the catalytic performance of Au catalyst were discussed in detail.

2. Experimental

2.1 Materials

$HAuCl_4 \cdot 4H_2O$ (Au content ≥ 47.8%) was purchased from Alfa Aesar company; $BaCl_2 \cdot 2H_2O$ was purchased from Tianjin Guangfu Technology Development Co., Ltd., and AC (pH = 5-7, coconut shell carbon, 20–40 mesh) was purchased from Fujian S. S. Activated Carbon Industry Science and Technology Co., Ltd. All the other materials and chemicals were commercially available and were used without further purification.

2.2 Catalyst preparation

Bimetallic Au-Ba(II)/AC catalysts were prepared using an incipient wetness impregnation method.[10-14] The raw material of activated carbon was treated with 1 mol L^{-1} HCl solution at 70 °C for 5 h to remove impurities (Na, Fe, etc),[14] and then washed with distilled water and dried at 150 °C for 12 h, the obtained sample is denoted as the activated carbon support in this work. A $HAuCl_4$ aqua regia solution was added dropwise to the activated carbon support under stirring, then the mixture was set aside for 10 h at room temperature, followed by evaporation at 60 °C for 10 h and adding quantitatively a $BaCl_2$ aqueous solution under stirring. The mixture was set aside, evaporated, and dried at 150 ℃ for 16 h to obtain the supported Au-Ba(II)/AC catalyst. The Au loading amount of all the catalysts was fixed at 1.0 wt%, and the bimetallic catalysts were denoted as Au1Ba(II)*x*/AC with the molar ratio

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x equal to 0.5, 1, 3,and 5 respectively. As a control, monometallic catalyst Au/AC (1.0 wt%) and Ba(II)/AC (1.0 wt% Ba) catalysts were also prepared through the same procedures described above.

On the other hand, the impregnation order of gold and barium precursors was reversed to prepare another bimetallic catalysts Ba(II)1Au1/AC, i.e., performing the first impregnation of $BaCl_2$ followed by that of $HAuCl_4$. The third kind catalyst co-Au1Ba(II)1/AC was prepared through co-impregnation of an aqueous solution of $HAuCl_4$ and $BaCl_2$, as shown in Fig. S1a. All these catalysts contained 1.0 wt% Au with a Ba/Au mole ratio of 1:1.

2.3 Catalytic performance tests

Activity tests were carried out in a fixed bed stainless steel microreactor (i.d., 10 mm), as described in previous works. [24, 27, 43] The temperature of the reactor was regulated by an intelligent precision controller programmer AI set produced by Yudian Automation Technology Co., LTD. (Xiamen, China).

A purge pipeline with nitrogen was used prior to the catalytic reaction to remove moisture and air in the system. Acetylene (gas, 98.0%) and hydrogen chloride (gas, 99.0%) were then fed into a heated reactor containing 5 mL of the catalysts to achieve a GHSV(C_2H_2) value of 360 h^{-1} (C_2H_2: 30.0 mL min^{-1}, HCl: 34.5 mL min^{-1}), after experienced the filtration to remove trace impurities. The effects of external and internal diffusions on the catalytic performance were eliminated at a flow rate range of 25–100 mL min^{-1} (C_2H_2) and a grain size range of 0.180–0.900 mm. The pressure of the reactants (HCl and C_2H_2) was maintained within the range of 0.11–0.12 MPa.

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After 4 h reaction to reach a steady state, the reactor effluent experienced the adsorption by NaOH solution to remove unreacted HCl were analyzed by gas chromatography (Shimadzu GC-2014C).

2.4 Catalyst characterization

Low-temperature N_2 adsorption/desorption experiments were conducted using a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Instruments, USA). The samples were first degassed at 150 °C for 6 h and analyzed via liquid nitrogen adsorption at −196 °C.

Thermogravimetric analysis (TGA) of the samples was performed using a NETZSCH TG 209 F3 TGA instrument in an air atmosphere at a flow rate of 80 mL min^{-1}. The temperature was increased from 40 to 800 °C at a heating rate of 10 °C min^{-1}.

X-ray diffraction (XRD) measurements were performed using a Rigaku D/max 2500 v/pc X-ray diffractometer with monochromatized Cu Kα radiation (λ=1.5406 Å) operating at 40 kV and 40 mA in the 2θ scan range between 10 and 90 (10 °min^{-1}). Particle size was determined using the Scherrer equation assuming spherical particle shapes and a K factor of 0.89.

Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments were performed using a TPDRO 1100 apparatus (Thermo-Finnigan) equipped with a thermal conductivity detector (TCD). The weight of the tested samples was 50 mg and 200 mg respectively for TPR and TPD experiments. Prior to each test, the samples were treated with N_2 gas at 60 ℃ for 0.5 h.

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After cooling, the temperature was increased from 20 to 900 ℃ at a heating rate of 10 ℃ min^{-1} with a 10.0% H_2/Ar atmosphere flowing at a rate of 40 mL min^{-1} for TPR and a N_2 atmosphere for TPD experiment.

3. Results and Discussion

3.1 Catalytic performance of bimetallic catalysts

Three kinds of bimetallic catalysts, Au1Ba(II)1/AC, Ba(II)1Au1/AC and co-Au1Ba(II)1/AC, prepared with different impregnation order of gold and barium precursors, were assessed for acetylene hydrochlorination reaction to study the effect of impregnation order on catalytic performance. As shown in Fig. S1b, the acetylene conversion is 96.3 % over Au1Ba(II)1/AC, 96.4 % over Ba(II)1Au1/AC and 90.6 % over co-Au1Ba(II)1/AC at 10 h, whereas after 48 h it decreases respectively to 94.8%, 89.3% and 86.7%. It is indicated that the impregnation order of two precursors indeed affects the initial catalytic activity of bimetallic catalysts, however, Au1Ba(II)1/AC, with the first impregnation of Au followed by that of Ba(II), has the best stability within 48 h reaction.

Then adopting the optimal impregnation order of Au following Ba(II) precursors, we prepared catalysts Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, 5) and assessed for acetylene hydrochlorination to study the effect of molar ratio Au/Ba on the catalytic performance. As shown in Fig. 1, the monometallic Ba(II)/AC shows the acetylene conversion of 24.0% at 48 h, which is close to that over the support AC. Over the monometallic Au/AC catalyst the acetylene conversion is 93.6% at 20 h and decreases to 85.6% at 48 h. While over bimetallic catalysts Au1Ba(II)*x*/AC, the acetylene

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conversion at 48 h is respectively 94.6 %, 97.2%, 92.3%, and 81.5% as the molar ratio Au/Ba(II) rises from 0.5 to 5. It is worthy to note that over the optimal Au1Ba(II)1/AC acetylene conversion still maintains a high acetylene conversion (92.3%) after 86 h reaction (Fig. S2). The selectivity to VCM over all these catalysts is greater than 99.0% (Fig. S3), and the addition of Ba(II) shows no negative effect on the selectivity. It is suggested that adding Ba(II) can improve the catalytic activity and the stability of gold catalysts for acetylene hydrochlorination.

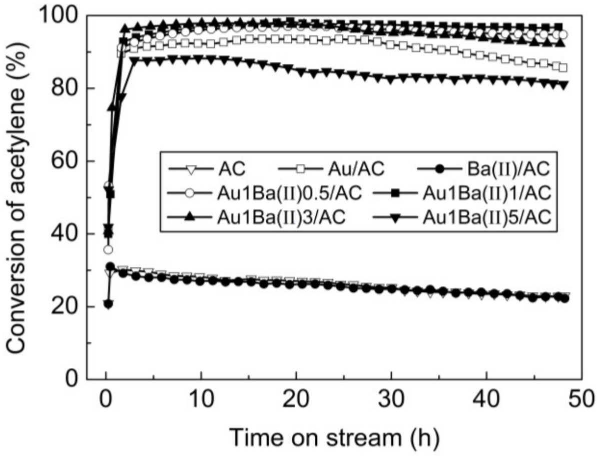

Fig. 1 Catalytic performance of Au-Ba(II)/AC catalysts. Reaction conditions: Temperature (T) = 200 ℃, GHSV(C_2H_2) = 360 h^{-1}, Feed volume ratio $V_{HCl}/V_{C_2H_2}$ =1.15.

3.2 Catalyst characterization

A series of characterization methods were carried out to disclose the structural and physicochemical properties of the bimetallic catalysts Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, or 5).

3.2.1 Effect of Ba(II) additive on the gold catalyst before the reaction

TPR profiles of catalysts Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, 5) display the peak centered at

268 °C, attributed to the reduction of Au^{3+} species,[17] together with the superimposed peak near 450 °C, as shown in Fig. 2. It is known that on surfaces of activated carbon there exist certain oxygenated groups,[48] and heteroatoms.[49] The reduction bands located higher than 350 ℃ are attributed to the interaction between metallic species and oxygenated groups involving carboxylic acids or carboxylic anhydrides on the support surfaces (Fig. 2).[50, 51] For the bimetallic catalysts with lower content of Ba(II), Au1Ba(II)0.5/AC and Au1Ba(II)1/AC, the reduction band of Au^{3+} shifts slightly towards lower temperature (259 °C). And the relative sharp peaks near 268 °C of Au1Ba(II)x/AC (x = 0.5, 1, 3, or 5) indicate that the addition of Ba(II) can make Au species dispersed well, compared with that of Au/AC. It is worth mentioning that the relative amount of Au^{3+} increases with the Ba(II)/Au ratio. Previous work suggested that both Au^{3+} and its reducibility are vital to improve the catalytic activity.[16] For Au1Ba(II)3/AC and Au1Ba(II)5/AC with higher content of Ba(II), excess amount of Ba(II) can partially cover active gold species, therefore the corresponding catalytic performance becomes poorer (Fig. 1). It is clear that a proper amount of Ba(II) additive, with the Au/Ba ratio of 1:1, can result in well dispersed Au^{3+} species, and consequently obtain excellent catalytic performance over Au1Ba(II)1/AC(Fig. 1).

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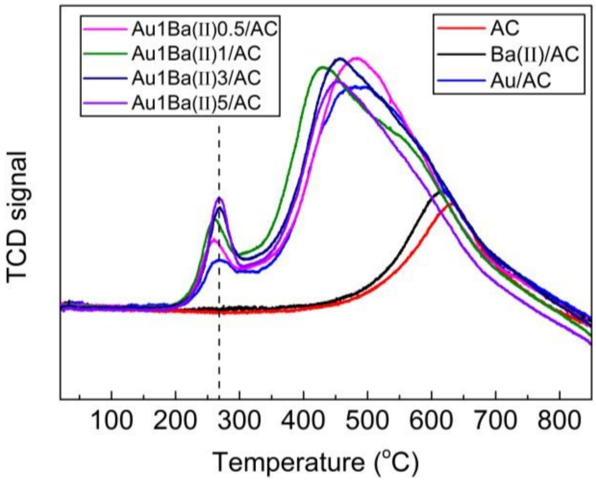

Fig. 2 H_2-TPR profiles of the fresh Au-Ba(II)/AC catalysts.

TPD measurements were carried out for bimetallic catalysts Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, or 5) to study the effect of Ba(II) additive on the adsorption properties of reactants (Fig. S4a). It is indicated that the desorption peaks of acetylene are centered approximately 440 ℃ for Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, 5). The calculated desorption area of acetylene decreases in the order of Au1Ba(II)1/AC > Au1Ba(II)5/AC > Au1Ba(II)3/AC > Au1Ba(II)0.5/AC > Au/AC, as listed in Table 1, suggesting that the addition of Ba(II) can enhance the adsorption of acetylene on catalysts.

For another reactant hydrogen chloride, the desorption peaks are broad bands in the range of 200-900 ℃ for Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, 5) (Fig. S4b), suggesting the existence of multi-status adsorbed HCl on the catalysts that cannot be desorbed as easily as adsorbed C_2H_2. The desorption area of hydrogen chloride gradually increases with the amount of Ba(II) additive, however, for Au1Ba(II)1/AC catalyst that exhibits the highest catalytic activity (Fig. 1), the desorption area of HCl is about one twentieth of that of C_2H_2 (Table 1). Previous literatures suggested that the acetylene

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hydrochlorination may involve the addition of HCl to a surface metal acetylene complex.[52-54] In combination with the catalytic performance of Au1Ba(II)*x*/AC (*x* = 0.5, 1, 3, 5), it is illuminated that Ba(II) additive with the Au/Ba ratio of 1:1 can enhance greatly the adsorption amount of acetylene and hydrogen chloride on the catalysts, but also promote much stronger interactions between adsorbed HCl and the catalysts.

Table 1 Desorption amount of C_2H_2 and HCl on the fresh catalysts.

Catalyst	Desorption area of C_2H_2	Desorption area of HCl
AC	750	980
Ba(II)/AC	921	0
Au/AC	26565	2392
Au1Ba(II)0.5/AC	52994	2297
Au1Ba(II)1/AC	73802	3555
Au1Ba(II)3/AC	61627	23371
Au1Ba(II)5/AC	63183	62881

3.2.2 Effect of Ba(II) additive on the gold catalyst during the reaction

3.2.2.1 Catalyst texture properties

N_2 adsorption/desorption experiments show that the specific surface areas and total pore volumes of the catalysts decrease after loading the active component (Table 2 and Fig. S5). This result may be caused by the phenomenon called the dilution effect.[43] The active species fill or block some of carrier pores, leading to a decrease of the Brunauer-Emmertt-Teller (BET) surface areas and total pore volumes. When the loading of the active component is increased, more pores of the carrier are filled or

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blocked by the active species, thus the BET surface area and the total pore volume are decreased. Surprisingly, the surface area and pore volume of fresh Au1Ba(II)5/AC are greater than other Au-Ba(II)/AC catalysts, however, it exhibits a lower activity, which may be explained that the excess Ba(II) species cover partially of Au species and accumulate around the pores of the carrier, forming some new pore structures or islands. After the reaction, the used catalysts feature surface areas and total pore volumes lower than those of fresh catalysts (Table 2). About 21.0% of the surface area of the AC catalyst is lost after 48 h reaction. Loading of Au on AC results in an slight increase in the variation amplitude of the catalyst BET surface area (21.4% reduction, ΔS_{BET}%); Addition of Ba(II) to the Au catalyst reduces the ΔS_{BET}% in the following order: Au1Ba(II)5/AC (37.5%) > Au1Ba(II)0.5/AC (15.3%) > Au1Ba(II)3/AC (13.2%) > Au1Ba(II)1/AC (9.5%). Changes in the total pore volume also show the same trend: Au1Ba(II)5/AC (34.5%) > Au/AC (19.4%) > AC (16.3%) > Au1Ba(II)0.5/AC (13.3%) > Au1Ba(II)3/AC (10.3%) > Au1Ba(II)1/AC (8.1%). The decrease in activity observed is apparently due, at least in part, to loss of the active surface area and not loss of the Au metal (Table S1). Loss of active surface areas may be attributed to the carbonaceous material deposition on the catalyst surface. The observed decrease in surface area may also be attributed to the Au-catalyzed acetylene hydrochlorination reaction.[38] A significant loss of surface area and pore volume of Au1Ba(II)5/AC after the reaction may be ascribed to the deposition of carbonaceous material or the collapse of the pore structures or islands. Therefore, the optimal atomic ratio for Au/Ba(II) is 1:1, at which the used catalyst may have the least carbon deposition.

Table 2 Pore structure parameters of catalysts.

Catalyst	S_{BET} (m^2 g^{-1})		Total pore volume (cm^3 g^{-1})	
	Fresh	Used	Fresh	Used
AC	1297	1021	0.875	0.570
Au/AC	958	753	0.546	0.440
Au1Ba(II)0.5/AC	978	829	0.543	0.471
Au1Ba(II)1/AC	939	850	0.531	0.488
Au1Ba(II)3/AC	918	797	0.515	0.462
Au1Ba(II)5/AC	1025	641	0.576	0.378

3.2.2.2 Carbon deposition on the used catalysts

TGA results show that neither the fresh nor the used Au/AC catalyst has a bitty loss of mass before 150 °C (Fig. 3a), indicating that few water adsorption on catalyst surface occurs. In the range of 150-450 °C, the fresh Au/AC catalyst exhibits a slow weight loss, reaching 1.6% (Table S2). When the temperature exceeds 500 °C, the catalyst rapidly decreases in weight because of AC burning.[55] On the contrary, the used Au/AC catalyst has a significant weight loss (5.5%) in the range of 150-450 °C, mainly due to the burning of carbon deposition on the catalyst surface.

Upon addition of Ba(II), the fresh Au1Ba(II)1/AC catalyst (Fig. 3b) also shows a bitty weight loss before 150 °C due to the desorption of few adsorbed water on the carrier surface, followed by a slow weight decrease in the range of 150-450 °C (shown in Table S3). When the temperature exceeds 450 °C, the catalyst has a quick weight loss, which is also mainly caused by the activated carbon combustion.

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Whereas the used Au1Ba(II)1/AC catalyst has a small fraction of weight loss (6.4%) within 150-400 °C. When the temperature continues to rise from 400 °C to 450 °C, the weight loss of the used catalyst is 2.8%, nearly equal to that of the fresh Au1Ba(II)1/AC catalyst (2.7%), indicating that most of the carbon deposited on the catalyst surface are burned off when the temperature is higher than 400 ℃.

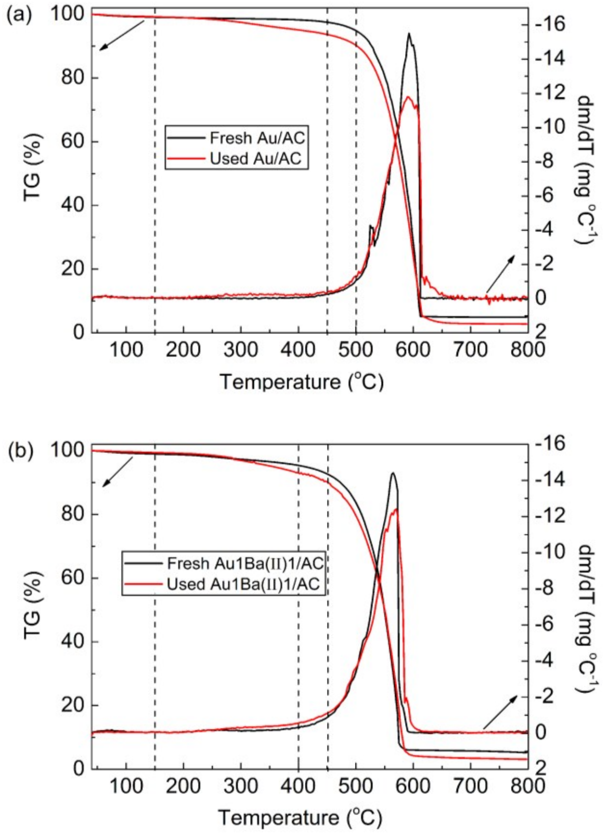

Fig. 3 TGA and DTG curves of the fresh and used Au/AC (a) and Au1Ba(II)1/AC (b) catalysts.

The amount of carbon deposition on the catalysts, calculated based on the above method, are listed in Table 3. The amount of carbon deposition on the Au/AC catalyst is the highest (4.7%). Carbon deposition resulted in clogged pores and reduced surface areas in the carrier, both of which decrease catalyst activity. The amount of carbon deposition is significantly reduced after addition of Ba(II) to the catalysts (Fig.

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S6); addition of this metal may separate the Au active sites on the surface of the catalysts and inhibited carbon deposition. The amount of carbon deposition on the catalysts shows the trend Au1Ba(II)1/AC (2.9%) < Au1Ba(II)5/AC (3.1%) < AC (3.4%) < Au1Ba(II)3/AC (3.5%) < Au1Ba(II)0.5/AC (3.6%) < Au/AC (4.7%). It is reasonable to conclude that the addition of Ba(II) is beneficial to inhibit the carbon deposition during the reaction.

Table 3 Carbon depositions on the Au-based catalysts.

Catalyst	Amount of carbon deposition (%)
AC	3.4
Au/AC	4.7
Au1Ba(II)0.5/AC	3.6
Au1Ba(II)1/AC	2.9
Au1Ba(II)3/AC	3.5
Au1Ba(II)5/AC	3.1

3.2.2.3 Catalyst sintering and the reduction of active component during the reaction

Fig. 4 displays the XRD patterns of the fresh and used Au-Ba(II)/AC catalysts. Apart from the amorphous diffraction peaks of AC, a discernible Au reflection is also detected at 38.36 ° in the fresh Au/AC catalyst (Fig. 4a), indicating that few large particles exist in the catalyst. After the addition of Ba(II), only an extremely weak peak can be seen from the pattern of Au1Ba(II)0.5/AC catalyst, and no discernible Au reflections are detected in the fresh catalysts as Ba(II) amount increases [Au1Ba(II)1/AC, Au1Ba(II)3/AC, and Au1Ba(II)5/AC; Fig. 4a], indicating particles

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below 4 nm or a material with a large amount of Au^{3+} centers.[16] TEM images confirm that Au species are well dispersed in the presence of Ba(II) additives [Fig. S7c and Table S4]. The used Au/AC clearly shows typical diffraction peaks of Au^0 at 38.36°, 44.56°, 64.83°, and 77.90° (2θ) (Fig. 4b), suggesting the change of Au valence (Au^{3+} is reduced into Au^0) or catalyst sintering during the reaction, so do the used bimetallic Au-Ba(II)/AC catalysts. The particle size of used Au/AC is 36 nm, calculated using the Scherrer equation, while it is 21 nm for Au1Ba(II)1/AC, as listed in Table S4. Therefore, the addition of Ba(II) can inhibit the sintering of Au particles in catalysts during the reaction.

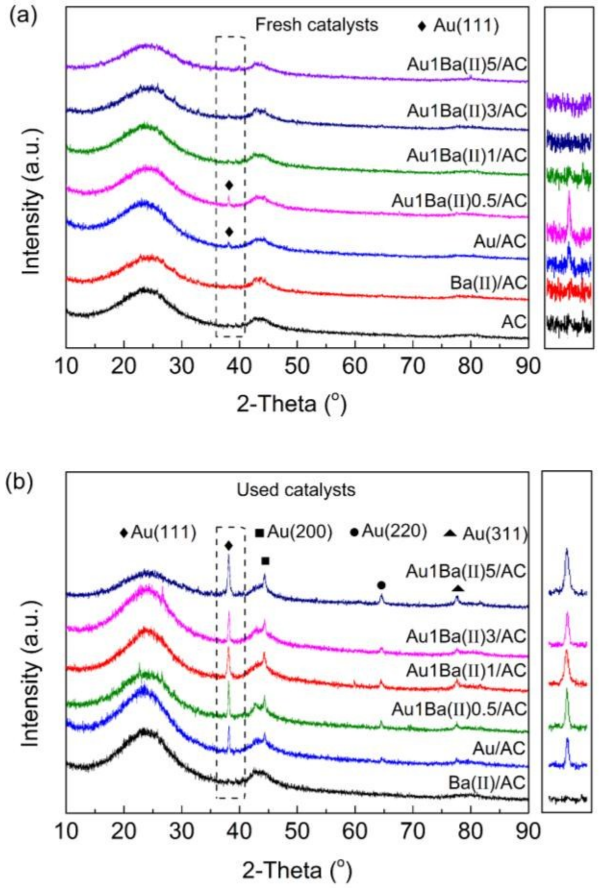

Fig. 4 XRD patterns of the fresh (a) and used (b) Au-Ba(II)/AC catalysts.

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Further, XPS spectra were analyzed to investigate the valence state and relative amount of the active species of bimetallic Au-Ba(II)/AC catalyst before and after reaction. It should be noted that the XPS spectra of Au 4f5/2 was overlapped with that of Ba (4d, 4d3/2, and 4d5/2), and the signals of Au 4d3/2 and 4d5/2 are very weak; thus, the Au 4f7/2 XPS spectra were analyzed to obtain the information of Au valence. There are more than one Au species appeared (Fig. S8), the curve fitting is employed to determine the ratio of each Au species.[17, 56] As listed in Table 4, for the fresh catalysts Au/AC and Au1Ba(II)0.5/AC, there are three gold species including Au^{3+}, Au^0 and metallic gold clusters of Au^0-s,[17, 57, 58] whereas for the fresh catalysts Au1Ba(II)*x*/AC(*x* = 1, 3, 5) there only exist Au^{3+} and Au^0, with the most abundance component of Au^0. Moreover, the presence of Ba(II) additives makes the peaks of Au^{3+} slightly shift to lower binding energy, while the peaks of Au^0 slightly shift to higher binding energy, confirming the strong interactions between gold and barium components. Electron transfer may occur between these species. The electron density around the Au^{3+} center is increased while that around the Au^0 center is decreased, enhancing the adsorption of hydrogen chloride and acetylene reactants, respectively.[26, 59, 60] This is consistent with the result of TPD analysis. In the case of used catalysts, over Au/AC the content of Au^{3+} decreases to zero but Au^0 increases to 75.4 %, whereas over Au1Ba(II)*x*/AC (*x*= 0.5, 1, 3, 5) there are three gold species of Au^{3+}, Au^0 and Au^0-s, with the Au^{3+} content in the range of 15 % ~23%. It is reported that the reduction of Au^{3+} into Au^0 results in the deactivation of Au-based catalysts.[3, 13, 15, 24] Therefore, it is illustrated that the addition of Ba(II) inhibits the reduction of Au^{3+} into

Au^0 in the preparation process but also during the reaction, which is consistent with the TPR results (Fig. 2). The strong interactions between gold and barium components can stabilize the high valence state of Au species during the reaction, consequently improving the activity and long-term stability of the catalysts.

Table 4 Relative content of Au species in the catalysts before and after reaction, determined by XPS.

Catalyst	Au species (%)			Binding energies (eV)		
	Au^{3+}	Au^0-s	Au^0	Au^{3+}	Au^0-s	Au^0
Fresh Au/AC	13.3	30.4	56.3	86.2	84.8	83.9
Used Au/AC	0	24.6	75.4	-	84.8	84.1
Fresh Au1Ba(II)0.5/AC	22.1	22.2	55.7	86.1	84.6	83.9
Used Au1Ba(II)0.5/AC	15.2	26.8	58.0	86.1	84.7	83.7
Fresh Au1Ba(II)1/AC	26.4	0	73.6	85.9	-	84.1
Used Au1Ba(II)1/AC	20.5	25.8	53.7	86.2	84.8	84.0
Fresh Au1Ba(II)3/AC	30.4	0	69.6	85.9	-	84.1
Used Au1Ba(II)3/AC	22.1	36.1	41.8	86.2	84.7	83.8
Fresh Au1Ba(II)5/AC	32.6	0	67.4	85.8	-	84.0
Used Au1Ba(II)5/AC	23.2	26.5	50.3	86.0	84.8	84.0

4. Conclusions

Several bimetallic gold-barium catalysts with different Au/Ba ratios were prepared and assessed for acetylene hydrochlorination. The best catalytic performance was obtained over Au1Ba(II)1/AC catalysts with the initial acetylene conversion of 98.4% and the selectivity to VCM of 99.9% under the conditions of temperature = 150 ℃, $V_{HCl}/V_{C_2H_2}$ = 1.15, and GHSV(C_2H_2) = 360 h^{-1}. Through characterizations of TPR, TPD, XRD, XPS, TGA, etc., it is illustrated that Ba(II) additive with the Au/Ba ratio

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of 1:1 can result in well dispersed Au^{3+} species, enhance greatly the adsorption amount of acetylene and hydrogen chloride on the catalysts, inhibit the reduction of Au^{3+} into Au^0 in the preparation process but also during the reaction. The strong interactions between gold and barium components can stabilize the high valence state of Au species during the reaction, consequently improving the activity and long-term stability of the catalysts.

Acknowledgements

We gratefully acknowledge financial support provided by the Major State Basic Research Development Program (No. 2012CB720302), the 863 Program (No. 2012AA062901), NSFC (21176174), and the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT1161).

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