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Strontium promoted activated carbon-supported gold catalysts for non-mercury catalytic acetylene hydrochlorination

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Abstract

Bimetallic gold-strontium catalysts were prepared and assessed the effect of Sr(II) additive on the catalytic performance of gold-based catalysts for acetylene hydrochlorination, combining with characterizations of N_2 adsorption/desorption, thermogravimetric analysis, temperature-programmed reduction/desorption, powder X-ray diffraction, transmission electron microscopy, atomic absorption spectrophotometer and X-ray photoelectron spectroscopy. The optimal catalytic performance is obtained over Au1Sr(II)1/AC catalyst with the acetylene conversion of 87.7% and the selectivity to VCM of 99.8% after 20 h on stream under the conditions of 180 °C, C_2H_2 gas hourly space velocity (GHSV) of 762 h^{-1}, and the feed volume ratio HCl/C_2H_2 of 1.15, which increases by 24.3% comparing with the acetylene conversion of 63.4% after 20 h on stream under the same conditions over the monometallic Au/AC catalyst. It is indicated that the addition of Sr(II) can make Au species dispersed well and inhibit carbon deposition on the catalyst surface; Sr(II) additive can enhance the adsorption of two reactants acetylene and hydrogen chloride on the catalysts and inhibit the reduction of Au^{3+} to Au^0 during the preparation and reaction, consequently enhancing the catalytic activity and long-term stability of gold-based catalysts.

Keywords: acetylene hydrochlorination; gold catalysts; strontium; heterogeneous catalysis

Introduction

Acetylene hydrochlorination is one of noticeable industrial processes to produce vinyl chloride monomer (VCM) in the polyvinyl chloride (PVC) industry, especially in coal-rich countries, the current industrial catalyst for this process is based on mercuric chloride supported on activated carbon (AC).[1–3] However, high toxicity and volatility of the active mercuric chloride component can cause serious environmental pollution, and then the non-friendly mercuric chloride industrial catalyst for this process will be prohibited by the United Nations in the near future[4, 5]. Thus, developing a high active and long stable non-mercury catalyst for acetylene hydrochlorination is very urgent.

Following the pioneering work of Hutchings[6], activated carbon-supported gold catalyst (Au/AC) as an efficient, environmentally friendly, and promising alternative non-mercury catalyst for acetylene hydrochlorination has attracted widespread interest[4, 5, 7–14]. Although the initial activity of the gold catalyst is higher than other supported metal chloride catalysts, including supported mercury chloride catalyst, but the deactivation rate of gold catalyst is much faster owing to the easy reduction of active Au^{3+} species and the serious carbon deposition during the reaction.[4, 9, 10, 13–15] Recently, some researchers have reported that the addition of metal additives can improve the catalytic performance of Au-based catalysts for acetylene hydrochlorination.[15–22] For examples, Wang *et al.* studied the effect of copper additive on the catalyst performance of Au-based catalysts and reported that the Au1Cu5/C catalyst (w/w, total metal amount of 3.0 wt%) promoted more than 99.5% acetylene conversion and more than 99.5% selectivity to VCM after 200 h of reaction under reaction conditions of 160 °C, GHSV (C_2H_2) of 50 h^{-1} and V_{HCl}/V_{C2H2} ratio of 1.15[16]. Zhang *et al.* studied the effect of La(III) and Co(III) additives on the performance of Au-based catalysts and reported that over the spherical activated carbon-supported Au1M3 catalysts [a/a, 1.0 wt% Au, and M = La(III), Co(III)] the acetylene conversion achieved 100% initially under the conditions of 150 °C, GHSV (C_2H_2) of 360 h^{-1} and V_{HCl}/V_{C2H2} ratio of 1.15, while after 48 h it decreased by 11% for Au–La(III) and 7% for Au–Co(III) catalyst respectively.[17, 18] Zhou *et al.* studied Au-Bi catalysts and found that the addition of Bi(III) could suppress the reduction of oxidation states of gold into metallic Au^0 and consequently promote the catalytic activity for acetylene hydrochlorination.[19] Huang *et al.* studied the effect of the nitrogen-containing ligand 1,10-phenanthroline on the performance of Au-based catalysts and reported that over the $[AuCl_2(phen)]Cl/AC$ catalyst (w/w, 0.49 wt% Au) the acetylene conversion was 90% after 40 h of reaction under the conditions of 180 °C, GHSV (C_2H_2) of 280 h^{-1} and V_{HCl}/V_{C2H2} ratio of 1.2.[23] Zhang and co-worker assessed the ternary Au–Co(III)–Cu(II) catalysts and reported that the acetylene conversion of the optimal catalyst Au1Co(III)3Cu(II)1/SAC reached 99.7% and the selectivity to VCM was 99.9% within 48 h under the reaction conditions of 150 °C, GHSV (C_2H_2) of 360 h^{-1}, and V_{HCl}/V_{C2H2} ratio of 1.15.[20] Despite these finding are encouraging, obtaining an effective and long-term stable non-mercury catalyst for acetylene hydrochlorination is still a great challenge.

Strontium as an effective promoter is widely studied in Au–Sr/TS-1 catalysts to increase both the gold content and catalytic activity for direct propylene epoxidation using H_2 and O_2[24], supported palladium catalysts (Pd–Sr/zeolite-β, Pd–Sr/Al_2O_3, Pd–Sr/SiO_2, Pd–Sr/hydrotalcite, and Pd–Sr/MgO) to improve both the hydrogen adsorption capacity and hydrogenation activity for phenol hydrogenation[25], and Co–Sr/γ-Al_2O_3 and Ni–Sr/γ-Al_2O_3 catalysts to enhance stability and inhibit the coke formation for dry reforming of methane[26]. These prompted us to consider whether or not the strontium additive can augment the catalytic performance of Au-based catalysts for acetylene hydrochlorination. In this paper, aiming to establish an efficient non-mercury catalyst, gold-strontium catalysts were prepared on activated carbon to study the effects of the gold and strontium precursors impregnation order and Au/Sr(II) molar ratio on the catalytic performance of gold catalysts for acetylene hydrochlorination, combined with characterizations of BET, TGA, TPR, XRD, TEM, and XPS, etc.

2. Experimental

2.1 Materials

$HAuCl_4 \cdot 4H_2O$ (Au assay ≥ 47.8%) was purchased from Sinopharm Chemical Reagent Co., Ltd, China; $SrCl_2 \cdot 6H_2O$ was purchased from Tianjin Guangfu Technology Development Co., Ltd; Activated carbon (AC, neutral, coconut carbon, 20–40 mesh) was supplied by S. S. Activated Carbon Industry Science and Technology Co., Ltd. All the other materials and chemicals were commercially available and were used without any purification.

2.2 Catalyst preparation

Bimetallic Au–Sr(II)/AC catalysts were prepared using an incipient wetness impregnation method. The raw activated carbon was first pretreated with 1 mol L^{-1} HCl solution at 70 °C for 6 h to remove Na, Fe, and Cu impurities, and then washed with deionized water until pH 7 and dried at 150 °C for 12 h. The obtained sample was denoted as the AC support in this study. A $SrCl_2$ aqueous solution was added dropwise to the pretreated AC support with agitated stirring, then the mixture was dipped for 10 h at room temperature, followed by evaporation at 60 °C for 8 h and adding quantitative a solution of $HAuCl_4 \cdot 4H_2O$ in *aqua regia* with agitated stirring. The mixture was dipped, evaporated, and then dried at 150 °C for 14 h and used as a catalyst. The obtained bimetallic catalysts were denoted as Au1Sr(II)x/AC (x= 0.5, 1, and 3) with the Au/Sr(II) molar ratio of 1:0.5, 1:1, and 1:3, respectively. As a control, Au/AC and 1Sr(II)/AC (the metallic Sr content is 1.0 wt%) were also prepared in the similar procedure. The amount of Au loading in all these catalysts was fixed as 1.0 wt%.

In addition, the other two kinds of bimetallic catalysts were also prepared by changing the impregnation order of gold and strontium precursors. As shown in Fig. S1, the second kind of Sr(II)1Au1/AC catalyst was prepared through the first impregnation of $HAuCl_4 \cdot 4H_2O$ in *aqua regia* on AC followed by that of $SrCl_2$ aqueous solution; the third kind of *co*-Au1Sr(II)1/AC catalyst was prepared by co-impregnation of an aqueous solution of $HAuCl_4 \cdot 4H_2O$ and $SrCl_2$ onto AC.

2.3 Catalytic performance evaluation

The catalytic performance of the samples was investigated using a fixed-bed glass microreactor (i.d. of 8 mm). The temperature of the microreactor was regulated by a CKW–1100 temperature controller produced by Chaoyang Automation Instrument Factory, Beijing, China. Acetylene (99.9 % purity) was passed through silica-gel desiccant to remove trace impurities, and hydrogen chloride gas (99.9 % purity) was dried using 5A molecular sieves. Acetylene (12.7 mL min^{-1}) and hydrogen chloride (14.6 mL min^{-1}) were introduced into a heated reactor containing catalyst (1 mL) through a mixing vessel via calibrated mass flow controllers giving a GHSV (C_2H_2) of 762 h^{-1} at 180 °C. In order to keep safety of evaluating the activity under mild conditions, the pressure of the reactants, both HCl and C_2H_2, was performed in the range of 1.1–1.2 bar. The reactor effluent was passed through an absorption bottle containing saturated sodium hydroxide solution to remove unreacted hydrogen chloride. Finally, the gas mixture was analyzed by Beifen GC–3420A gas chromatograph.

2.4 Catalyst characterization

Low-temperature N_2 adsorption/desorption experiments were performed using a Micromeritics ASAP 2020C surface area analyzer. The catalysts and AC support were first degassed at 150 °C for 6 h and then analyzed via liquid nitrogen adsorption at –196 °C.

The gold content in all catalysts was measured using an air–acetylene flame atomic absorption spectrophotometer (Perkin–Elmer, AAS 800) according to the recommended conditions.

Thermogravimetric analysis (TGA) of the catalysts and AC support was carried out using a TA Instruments SDT Q600 under air atmosphere at a flow rate of 100 mL min^{-1}. The weight of all these samples was fixed as 5 mg. The temperature was increased from 35 to 900 °C at a heating rate of 10 °C min^{-1}.

Powder X-ray diffraction (XRD) measurements were carried out with a Bruker D8 Focus diffractometer using Cu Kα radiation with 4° min^{-1} scan speed and 20–80° scan range at 40 kV and 40 mA.

H_2 temperature-programmed reduction (TPR) and He temperature-programmed desorption (TPD) experiments were conducted using a Micromeritics AutoChem II 2920 analyzer equipped with a thermal conductivity detector (TCD). The weight of the tested samples was 50 mg and 100 mg respectively for TPR and TPD studies. Prior to each test, the samples were first pretreated with N_2 gas at 100 °C for 1 h. After cooling, the temperature was increased from 50 to 800 °C at a heating rate of 10 °C min^{-1} with a 10.0 % H_2/Ar atmosphere flowing at a rate of 20 mL min^{-1} for TPR and a He atmosphere for TPD experiments.

Transmission electron microscopy (TEM) was performed on a JEM 2100F field emission transmission electron microscope (JEOL, Tokyo, Japan) working at 200 kV using a scanning TEM mode. As for sample preparation, the samples were first ground in an agate mortar and ultrasonically dispersed in anhydrous ethanol, and then a drop was deposited on a carbon-coated copper grid and dried. The particle size distribution of Au nanoparticles on the fresh and used catalysts were observed by TEM images and determined from a count of 200 particles.

X-ray photoelectron spectra (XPS) were obtained using a PHI 5000 Versaprobe (ULVAC–PHI Inc., Osaka, Japan) employing monochromatic Al Kα X-rays source (hν = 1486.7 eV, 27.3 W) under high vacuum condition. The data were collected at a sample tilt angle of 45°, scanning step of 0.1 eV and spot diameter of 100 μm. The binding energies were corrected using the C 1s peak of aliphatic carbon at 284.8 eV as an internal standard.

3. Results and discussion

3.1 Catalytic performance for acetylene hydrochlorination

In order to determine the optimal impregnation order of the gold and strontium precursors, three kinds of bimetallic catalysts, Sr(II)1Au1/AC, Au1Sr(II)1/AC, and *co*-Au1Sr(II)1/AC were prepared and assessed for the acetylene hydrochlorination to investigate the effect of impregnation order on catalytic performance. As shown in Fig. S2, the initial acetylene conversion is 75.3% over Sr(II)1Au1/AC, 88.3% over Au1Sr(II)1/AC and 65.3% over *co*-Au1Sr(II)1/AC at 10 h, whereas it decreases respectively to 73.1%, 87.7% and 51.4% after 20 h of reaction. This indicates that the impregnation order of the gold and strontium precursors has a great influence on the initial catalytic activity of the bimetallic catalysts, comparatively speaking, Au1Sr(II)1/AC catalyst, with first impregnation Sr(II) followed by impregnating with Au(III), shows the optimal catalytic activity for acetylene hydrochlorination within 20 h of reaction.

Then, we prepared the bimetallic catalysts Au1Sr(II)x/AC (x = 0.5, 1, 3) using the optimal impregnation order of first Sr(II) following Au(III) precursors and studied the effect of the Au/Sr(II) molar ratio on the catalytic performance for acetylene hydrochlorination. As shown in Fig. 1a, the acetylene conversion is respectively 6.4% over the blank support AC, 6.0% over 1Sr(II)/AC, and 71.5% over the monometallic Au/AC catalyst at 10 h, but it decreases respectively to 5.4%, 5.1% and 63.4% after 20 h of reaction. This result demonstrates that AC and 1Sr(II)/AC display very poor catalytic activity for acetylene hydrochlorination. Over the bimetallic catalysts Au1Sr(II)x/AC (x = 0.5, 1, 3), with the increase of Sr(II)/Au molar ratio from 0.5 to 3, the acetylene conversion is respectively 82.1%, 88.3%, and 85.1% at 10 h, whereas it decreases respectively to 73.0%, 87.7% and 82.6% after 20 h. As shown in Fig. 1b, all these samples illustrate that the selectivity to VCM exceeds 99.0%. It is worth noting that the Au1Sr(II)1/AC catalyst demonstrates the optimal catalytic performance for acetylene hydrochlorination in the several kinds of catalyst samples, and the acetylene conversion is higher than the values previously reported in the literature about Au-based catalysts.[7, 11, 12] However, with much higher content of Sr(II) additive, the Au1Sr(II)3/AC catalyst shows a little lower acetylene conversion than Au1Sr(II)1/AC. The turnover frequency (TOF) values of the representative Au/AC and Au1Sr(II)1/AC catalysts were calculated to be 2.0 and 2.8 s^{-1} (Table S1), and the value was higher than that of the 1Au–4Cs^{I}/AC catalyst reported by Zhao *et al.*[21]. These results indicate that the Sr(II) additive can improve the catalytic activity and the stability of Au-based catalysts for acetylene hydrochlorination, but the excessive Sr(II) additive may tend to clog the pore and decrease the active surface area, and then leading to a decrease of catalytic activity (Fig. 1).

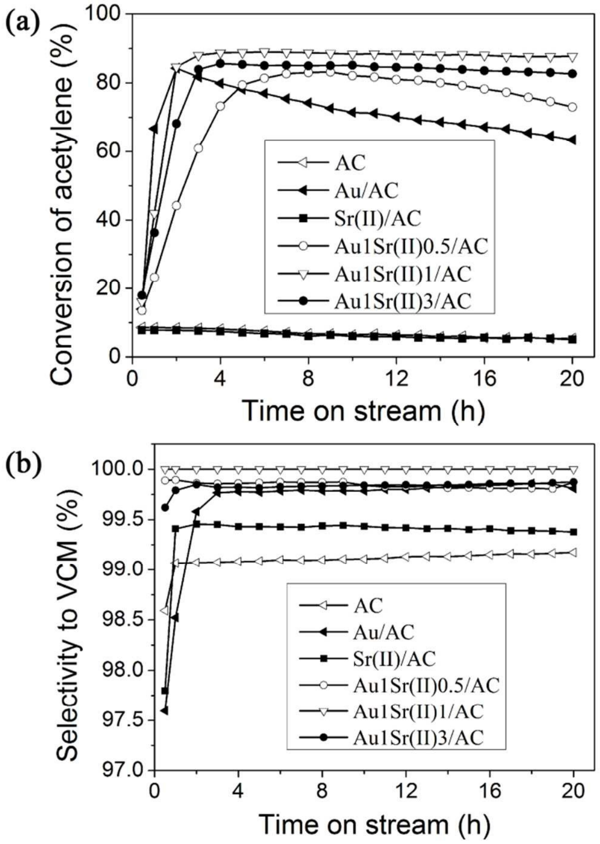

Fig. 1 Catalytic performance of Au–Sr(II)/AC catalysts. Reaction conditions: temperature (T) = 180 °C, GHSV (C_2H_2) = 762 h^{-1}, feed volume ratio V_{HCl}/V_{C2H2} = 1.15.

The long-term stability is crucial for the industrial application of acetylene hydrochlorination. To display the superior performance of Au1Sr(II)1/AC catalyst, we choose the typical Au/AC and Au1Sr(II)1/AC catalysts to further investigate the stability of the catalysts under the reaction conditions of 180 °C and GHSV (C_2H_2) of

60 h^{-1} over 300 h for the acetylene hydrochlorination. The Au1Sr(II)1/AC catalyst shows the acetylene conversion higher than 99.9% and the selectivity to VCM higher than 99.9% without any decline during 300 h test, as shown in Fig. S3. While for the Au/AC catalyst, the conversion of C_2H_2 decreased from the initial activity 99.9% to 95.6% after 300 h of reaction under the same reaction conditions. This indicates that the Au1Sr(II)1/AC catalyst can prove superior activity and stability.

3.2 Catalyst characterization

A series of characterization techniques were carried out to reveal the structure and physicochemical properties of the bimetallic Au–Sr(II)/AC catalysts.

3.2.1 Effect of Sr(II) additive on the texture property and amount of carbon deposition of gold catalysts

Low temperature N_2 adsorption/desorption experiments were used to measure the structure changes of gold catalysts caused by the addition of Sr(II). As shown in Table 1, the specific surface areas and total pore volumes of the fresh catalysts decrease after loading the active Au species and Sr(II) additive, which due to the active Au species and the Sr(II) additive fill or block some of AC pores. When the amount of Sr(II) additive increases, more AC pores are filled or blocked, the specific surface areas and total pore volumes of the fresh catalysts decrease accordingly. This phenomenon may be caused by the dilution effect. After 20 h of reaction, the used catalysts display lower specific surface areas and total pore volumes than those of the corresponding fresh catalysts, probably due to pore blocking caused by carbon deposition. Table 1 shows that the specific surface area and total pore volumes of the used Au/AC catalyst lost 23.0% and 22.9%, respectively. The addition of Sr(II) additive to gold catalysts decreases the variation trend of BET specific surface area (ΔS_{BET}%) after 20 h of reaction in the following order: Au1Sr(II)0.5/AC (15.3%) > Au1Sr(II)3/AC (13.0%) > Au1Sr(II)1/AC (10.9%). The total pore volumes of the used catalysts also show the same trends: Au/AC (22.9%) > Au1Sr(II)0.5/AC (15.3%) > Au1Sr(II)3/AC (13.0%) > Au1Sr(II)1/AC (11.0%). As determined by AAS, the used catalysts have no apparent variation of Au loading content (Table S2). The decrease of catalytic activity, at least in part, is owing to the loss of active specific surface area of Au–Sr(II)/AC, in particular, with the Sr(II)/Au molar ratio of 1:1, the reduce extent of the specific surface area is the least, accordingly corresponding to the highest activity over Au1Sr(II)1/AC catalyst (Fig. 1).

Table 1 Pore structure parameters of catalysts.

Catalyst	S_{BET} (m^2 g^{-1})		Total pore volume(cm^3 g^{-1})	
	Fresh	Used	Fresh	Used
AC	1126	/	0.639	/
Au/AC	1047	806	0.588	0.453
Au1Sr(II)0.5/AC	991	839	0.557	0.472
Au1Sr(II)1/AC	957	853	0.538	0.479
Au1Sr(II)3/AC	931	810	0.523	0.455

TGA was performed to investigate the amount of deposited coke on the surface of the used Au–Sr(II)/AC catalysts after 20 h of reaction under air atmosphere. Fig. S4 shows the representative TG and DTG curves of the fresh and used Au/AC and Au1Sr(II)1/AC catalysts. As seen in Fig. S4a, the fresh and used Au/AC catalysts have no apparent weight loss before 150 °C, indicating that a small amount of water adsorption on the catalyst surface occurs. In the range of 150–500 °C, the fresh Au/AC catalyst shows a slow weight loss, reaching 16.19%. At the temperature over 500 °C, a rapid decrease in the loss of weight can be ascribed to the burning of AC support.[27] As a comparison, the used Au/AC catalyst demonstrates a substantial weight loss (19.68%) in the range of 150–500 °C, which is mainly owing to the burning of deposited coke on the surface of the used Au/AC catalyst. Thus, the fresh Au/AC catalyst presents a weight loss of 16.19% in the range of 150–500 °C, indicating a weight loss of 16.19 g per 100 g of Au/AC sample; while for the used Au/AC catalyst the weight loss in the same temperature range is 19.68%, indicating a weight loss of 19.68 g per 100 g of (Au/AC catalyst + coke). Assuming that the amount of deposited coke on the used Au/AC catalyst equals X, the following equations should be satisfied, $100 / 16.19 = (100-X)/ Y$, and, $Y + X = 19.68$.

Then, the value of X is solved to be 4.16%. Therefore, the actual amount of deposited coke on the surface of the used Au/AC catalyst is 4.16%.

Upon the addition of Sr(II) with the optimal Sr(II)/Au molar ratio of 1:1, as shown in Fig. S4b, the fresh and used Au1Sr(II)1/AC catalysts display respectively the weight loss of 16.19% and 17.78% in the range of 150–500 °C. Similarly, the amount of deposited coke over the used Au1Sr(II)1/AC catalyst is calculated as 1.90%, which is the lowest, as listed in Table 2. It is apparent that the amount of deposited coke on the surface of the used Au/AC catalyst is highest, following the order of Au/AC (4.16%) > 1Sr(II)/AC (2.91%) > Au1Sr(II)0.5/AC (2.65%) > Au1Sr(II)3/AC (1.96%) > AC (1.92%) > Au1Sr(II)1/AC (1.90%). These results suggest that the amount of deposited coke over the Au–Sr(II)/AC catalysts is noticeably decreased by the addition of Sr(II). Here it is worth noting that the amount of deposited coke on the used Au1Sr(II)3/AC catalyst is higher than that on Au1Sr(II)1/AC, suggesting that the excessive Sr(II) additives produce more carbon deposition on the catalyst surface. The deposition of carbonaceous material on the used catalyst surface results in blocking pores and decreases specific surface area, and then reducing the catalytic activity, in accordance with the activity results in Fig. 1.

Table 2 Carbon depositions on the Au–based catalysts.

Catalyst	Amount of carbon deposition (%)
AC	1.92
Sr(II)/AC	2.91
Au/AC	4.16
Au1Sr(II)0.5/AC	2.65
Au1Sr(II)1/AC	1.90
Au1Sr(II)3/AC	1.96

3.2.2 Effect of Sr(II) additive on the reducibility and adsorption property of gold catalysts.

The TPR profiles were carried out to evaluate the reducibility of the fresh Au–Sr(II)/AC catalysts. A wide overlapping peak from 400 to 800 °C for all the samples is displayed in Fig. 2, which is attributed to the removal process of oxygenated carbon functional groups involving carboxylic acids and carboxylic anhydrides on activated carbon surfaces.[15, 28, 29] TPR profiles of the Au-based catalysts, as shown in Fig. 2, indicate that the Au/AC catalyst has a broad band near the temperature of 358 °C, attributed to the reduction of Au^{3+} species,[19] while the Au1Sr(II)0.5/AC, Au1Sr(II)1/AC and Au1Sr(II)3/AC catalysts have the reduction peak respectively at 358 °C, 350 °C and 357 °C. Comparing Au1Sr(II)1/AC with Au/AC, it is suggested that the size of gold particles in the Au1Sr(II)1/AC catalyst is smaller than that in Au/AC, resulting in the clear decrease of the peak temperature, which is proved by the following TEM images (Fig. 3).

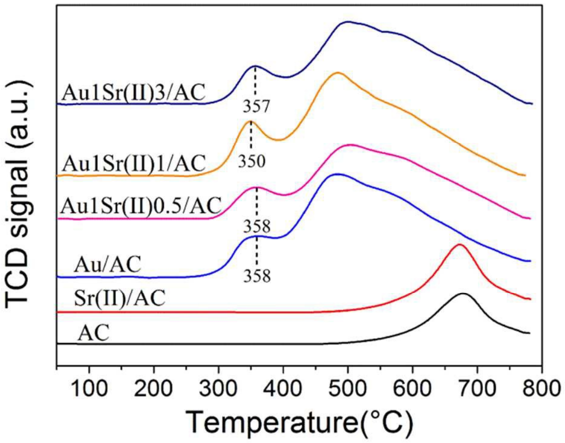

Fig. 2 H_2-TPR profiles of AC support and the fresh Au–Sr(II)/AC catalysts.

TEM images were observed to study the effect of Sr(II) additives on the dispersion of gold. Fig. 3 shows the typical TEM images and the particle size distributions of the fresh Au/AC and Au1Sr(II)1/AC catalysts. For the Au/AC catalyst, as shown in Fig. 3a and 3c, gold nanoparticles on the surface of activated carbon support have an average particle size about 2.95 nm, determined from a count of 200 particles in TEM images. While for the Au1Sr(II)1/AC catalyst, the gold nanoparticles are highly dispersed on the surface of the fresh Au1Sr(II)1/AC catalyst with an average particle size about 1.43 nm (Fig. 3b, 3d). The high dispersion of gold species can provide more active sites to catalyze the acetylene hydrochlorination reaction, consequently resulting in high catalytic activity (Fig. 1).

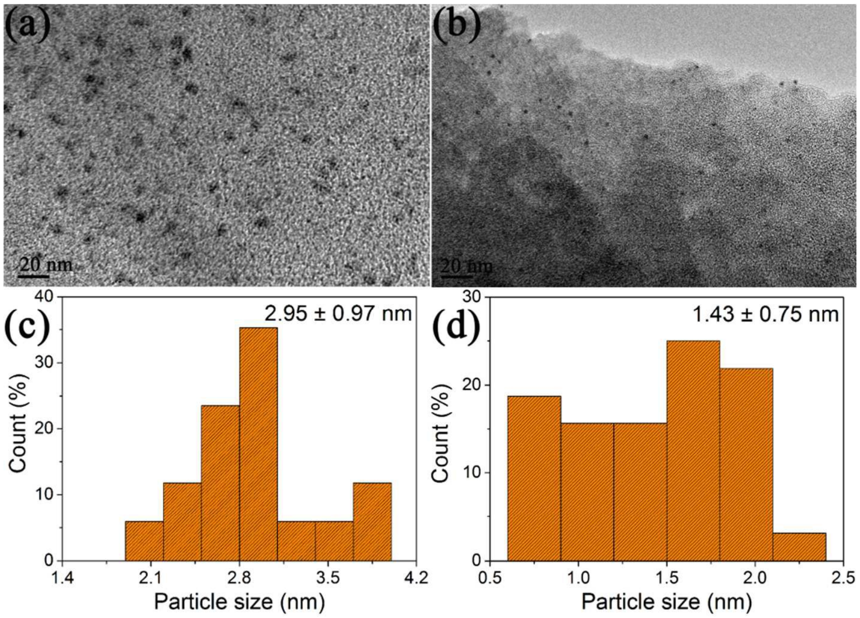

Fig. 3 TEM images of the fresh Au/AC catalyst (a), and the fresh Au1Sr(II)1/AC catalyst (b); and the particle size distribution of the fresh Au/AC catalyst (c), and the particle size distribution of the fresh Au1Sr(II)1/AC catalyst (d).

TPD experiments were used to examine the effect of Sr(II) additive on the adsorption properties of two reactants, acetylene and hydrogen chloride, over the fresh Au1Sr(II)x/AC (x = 0.5, 1, 3) catalysts. As shown in Fig. 4a, the fresh Au/AC catalyst displays two obvious acetylene desorption peak between 180 and 600 °C. While for the fresh Au1Sr(II)x/AC (x = 0.5, 1, 3) catalysts, the acetylene desorption peak is fairly broad and ill-defined shape in the range of 250–600 °C. It is obvious that the desorption peak area of the fresh Au1Sr(II)x/AC (x = 0.5, 1, 3) catalysts is larger than the fresh Au/AC catalyst. For another reactant hydrogen chloride, as shown in Fig. 4b, the fresh Au1Sr(II)x/AC (x = 0.5, 1, 3) catalysts show larger desorption area and higher desorption peak temperature than that of the Au/AC catalyst in the range of 120–600 °C. The desorption area of hydrogen chloride gradually increases with the amount of Sr(II) additive. It is obvious that the desorption area of the Au1Sr(II)1/AC catalyst is somewhat larger than that of the Au/AC catalyst, in accord with the higher initial acetylene conversion of Au1Sr(II)1/AC. The adsorption of hydrogen chloride is affected by the electron density of Au^{3+} center, the enhanced adsorption capacity of hydrogen chloride on the Au1Sr(II)1/AC catalyst may be related with the interaction relationship between Au^{3+} active centers and Sr(II) species. The results indicate that the addition of Sr(II) can improve the adsorption of two reactants acetylene and hydrogen chloride on the Au-based catalysts, in particular, with the Sr(II)/Au molar ratio of 1:1, the adsorption of both reactants hydrogen chloride and acetylene on the Au-based catalyst is the highest, consistent with the highest catalytic activity over Au1Sr(II)1/AC in Fig. 1.

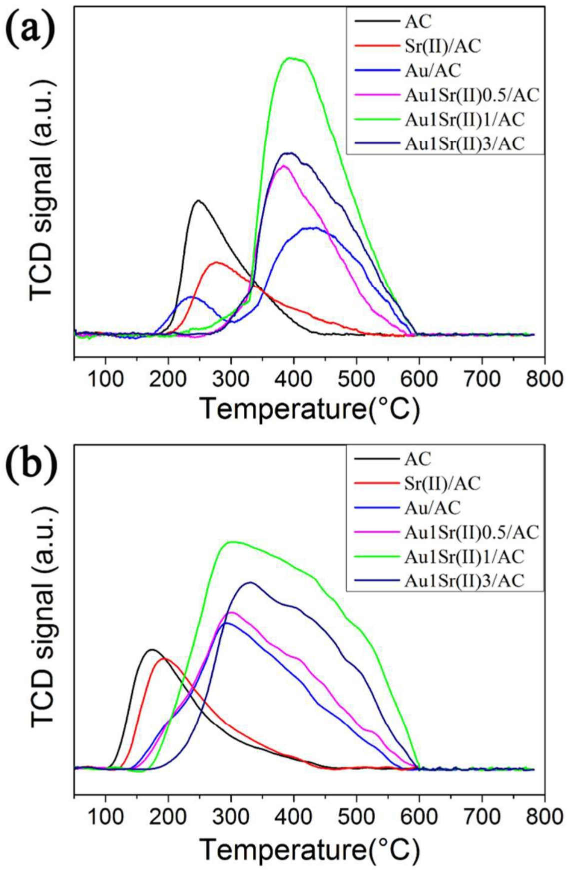

Fig. 4 (a) C_2H_2- and (b) HCl- TPD profiles of the fresh Au–Sr(II)/AC catalysts.

3.2.3 Effect of Sr(II) additive on catalyst sintering and valence change of the active component of gold during the reaction

Fig. 5 displays the typical XRD patterns of the fresh and used Au–Sr(II)/AC catalysts. It is worth noting that no obvious Au diffraction peaks can be observed in the fresh Au/AC catalyst in addition to the amorphous diffraction peaks of activated carbon (JCPDS 75–1621), indicating gold particles below 4 nm or a material with large amount of Au^{3+} centers[14]. Compared to the fresh Au/AC catalyst, the typical diffraction peaks are displayed at 38.04^0, 44.16^0, 64.54^0 and 77.74^0 (2θ) over the used Au/AC catalyst, which respectively assigned to the (111), (200), (220), and (311) planes of face-centered cubic (fcc) metallic Au^0 (JCPDS 04–0784), suggesting that a change of Au^{3+} valence (Au^{3+} is reduced to Au^0) and catalyst sintering occurs during the reaction, as shown in Fig. 5. The crystallite size of the Au nanoparticles is about 10 nm for the used Au/AC catalyst, calculated by the Scherrer equation using the Au(111) diffraction peak, while the fresh Au/AC catalyst displays a size less than 4 nm, as listed in Table S3, which is consistent with the TEM images (Fig. 3c, 6c). For the fresh and the used Au1Sr(II)1/AC catalysts, apart from the amorphous diffraction peaks of AC (JCPDS 75–1621), no Au diffraction peak can be detected. As shown in Table S3, the crystallite size of Au nanoparticles is less than 4 nm for both the fresh and used Au1Sr(II)1/AC catalysts, in accordance with the TEM images (Fig. 3d, 6d). It is suggested that the addition of Sr(II) can greatly inhibit the reduction of Au^{3+} into Au^0 and suppress the sintering of gold nanoparticles during the reaction.

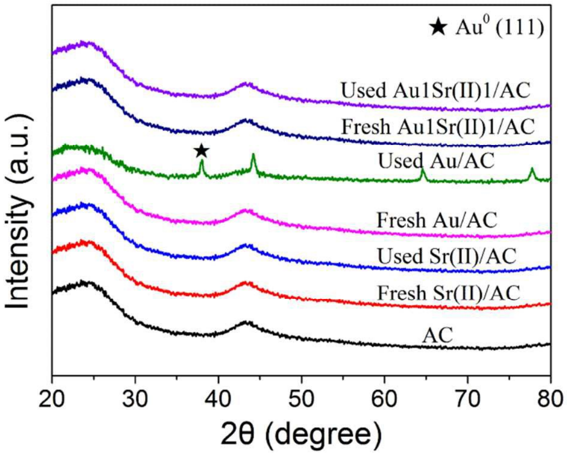

Fig. 5 Typical XRD patterns of AC support and the Au–Sr(II)/AC catalysts.

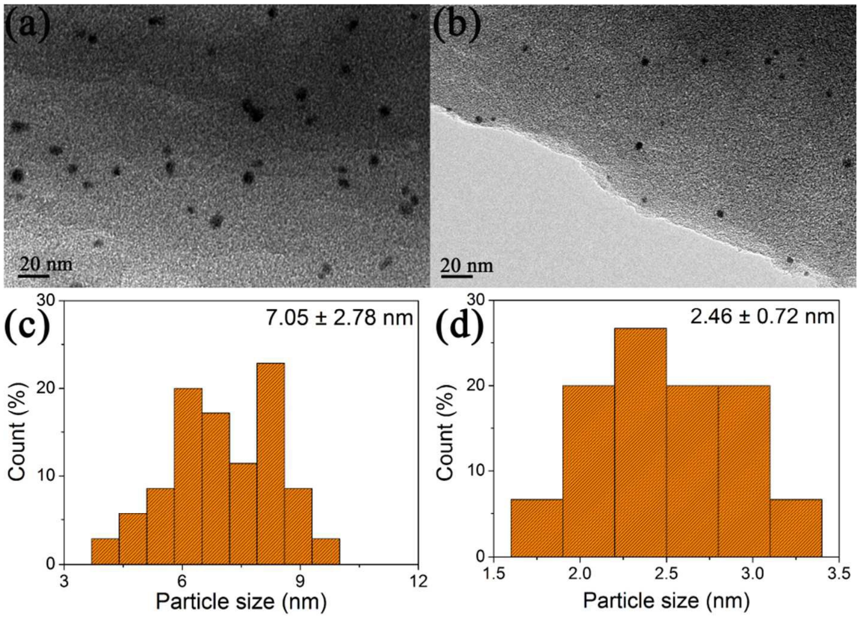

Fig. 6 TEM images of the used Au/AC catalyst (a), and the used Au1Sr(II)1/AC catalyst (b); and the particle size distribution of the used Au/AC catalyst (c), and the particle size distribution of the used Au1Sr(II)1/AC catalyst (d).

The valence state and relative content of active gold species in the typical Au/AC and Au1Sr(II)1/AC catalysts were studied through the analysis of the XPS data. Fig. S5 shows the high-resolution XPS spectra of Au 4f over the representative Au/AC and Au1Sr(II)1/AC catalysts before and after reaction. It is obvious that there are more than one gold species, and then the ratio of each gold species in total gold amount of the typical catalysts is determined by curve fitting analysis.[4] For all samples, as shown in Fig. S5, there are three kinds of Au species, involving metallic Au^0, small metallic gold clusters of Au^0-s and Au^{3+}.[4, 30, 31] Table 3 lists the binding energy and relative content of each gold species in different catalysts. It is indicated that in the presence of Sr(II) additive the binding energy of Au^{3+} is reduced by 0.2 eV, while that of Au^0 is increased by 0.2 eV, which suggests that electron transfers occur between gold active sites and strontium species, leading to an increase of electron density around the Au^{3+} center but a decrease of electron density around the metallic Au^0 species. Thus, there is a strong interaction between gold active sites and strontium species.

In addition, there are great content variations of gold species in the used catalysts. The content of Au^{3+} and Au^0 in the used Au/AC catalyst is respectively 14.0% and 72.6%, whereas those are 21.1% and 54.3% in the fresh Au/AC catalyst. In the case of Au1Sr(II)1/AC, after reaction the content of Au^{3+} decreases from 25.5% to 23.0% but the content of Au^0 increases from 58.7% to 59.4%. In the recent literature, the reduction of Au^{3+} to metallic Au^0 leads to the deactivation of Au-based catalysts for acetylene hydrochlorination.[3, 11, 13, 15, 22, 35, 36] Therefore, this indicates that Sr(II) additive can partially inhibit the reduction of active component Au^{3+} into metallic Au^0 during the catalyst preparation and the acetylene hydrochlorination reaction, and consequently enhance the catalytic activity for acetylene hydrochlorination (Fig. 1).

Table 3 The relative content and binding energy of Au species in fresh and used catalysts, determined from the deconvolution of Au 4f XPS spectra.

Catalyst	Au species (Area %)			Binding energies (eV)		
	Au^{3+}	Au^0-s	Au^0	Au^{3+}	Au^0-s	Au^0
Fresh Au/AC	21.1	24.6	54.3	86.4	84.9	83.9
Used Au/AC	14.0	13.4	72.6	86.4	85.0	84.0
Fresh Au1Sr(II)1/AC	25.5	15.8	58.7	86.2	84.9	84.1
Used Au1Sr(II)1/AC	23.0	17.6	59.4	86.2	84.9	84.1

4 Conclusion

Gold–strontium catalysts with different Au/Sr(II) molar ratio were prepared using activated carbon as the support and Sr(II) as an additive, and assessed for acetylene hydrochlorination. The optimal catalytic performance is achieved over Au1Sr(II)1/AC catalyst with the acetylene conversion of 87.7% and the selectivity to VCM of 99.8% after 20 h on stream under the conditions of 180 °C and GHSV (C_2H_2) of 762 h^{-1}, which increases by 24.3% comparing with the acetylene conversion of 63.4% after 20 h on stream under the same conditions over the monometallic Au/AC catalyst. Characterized through BET, AAS, TGA, TPR, TEM, TPD, XRD, and XPS, it is indicated that the addition of Sr(II) additive can make Au species dispersed well and inhibit carbon deposition on the catalyst surface; Sr(II) additive can enhance the adsorption of two reactants acetylene and hydrogen chloride on the catalysts and inhibit the reduction of Au^{3+} to Au^0 during the preparation and reaction, consequently augmenting the activity and long-term stability of gold-based catalysts.

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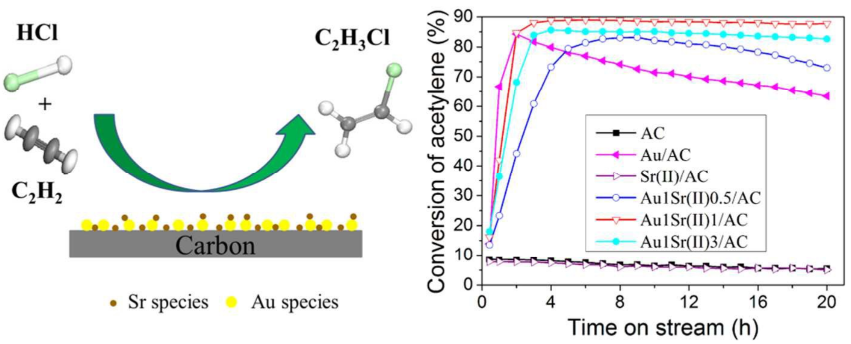
Graphical Abstract



Gold-strontium catalysts were prepared to assess the effect of Sr(II) additive on the catalytic performance of gold-based catalysts for acetylene hydrochlorination, using activated carbon as the support.