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Activated carbon supported ternary Gold-Cesium(I)-Indium(III) catalyst for the hydrochlorination of acetylene

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Abstract: Commercialization of acetylene hydrochlorination using $AuCl_3$ catalysts has been impeded by its poor stability. We have been studying CsCl as a promoter, which can improve acetylene hydrochlorination activity as well as have resistance to catalytic deactivation. In^{III}-added to the Au-[10] Cs^I/AC catalysts worked as efficient catalysts for the hydrochlorination of acetylene to vinyl chloride. A series of trimetallic catalysts ($1Aux In^{III} 4Cs^I$/AC with x = 0.5, 1, 2, 3) were prepared and assessed for their ability to promote hydrochlorination of acetylene. The enhancement of stability observed for $Au/In^{III}/Cs^I$ weight ratio of 1:1:4 was particularly remarkable. It delivered a stable performance within the conversion of acetylene, reaching more than 92.8% and there was only 3.7% C_2H_2 conversion loss after 50 h running [15] under the reaction conditions of temperature 180 °C and C_2H_2 hourly space velocity of 1480 h^{-1}. Moreover, the $1Au1In^{III}4Cs^I$/AC catalyst delivered a stable performance with an estimated lifetime exceeding 6520 h at C_2H_2 hourly space velocity of 50 h^{-1}. H_2-TPR, TEM, HCl-TPD, C_2H_2-TPD, XPS and TGA techniques were further applied to reveal the structural information on the $Au-In^{III}-Cs^I$/AC catalysts. The results reveal that the addition of $InCl_3$ increased the electron density of Au^{3+} species via electron [20] transfer from In atoms to Au^{3+} center can increase the adsorption of hydrogen chloride and therefore improve the catalytic stability. These results demonstrate that the addition of metal additives CsCl and $InCl_3$ results in a synergistic effect to enhance the activity and the stability of Au-based catalysts. The excellent catalytic performance of the $1Au1In^{III}4Cs^I$/AC catalyst demonstrated its potential as an alternative to mercury chloride catalysts for acetylene hydrochlorination.

Introduction

[25] Over the past decade, the hydrochlorination of acetylene has received significant attention as an alternative to manufacturing vinyl chloride monomers (VCM) in many developing countries, including China. This is because of the vast domestic coal [30] resources and increasing cost of petroleum.[1] Industrially, the hydrochlorination of acetylene is carried out using toxic carbon-supported mercuric chloride ($HgCl_2$) catalysts. However, $HgCl_2$ is apt to be reduced by acetylene and sublimates during reaction. This leads to the deactivation of the catalyst, contaminates the [35] product, and may cause severe environmental problems including threats to human health.[2] Thus, from a sustainable point of view, the replacement of $HgCl_2$ with a green metal catalyst is highly desirable for practical use.

Since their discovery by Hutchings[3], $AuCl_3$ has been the focus [40] of mercuric-free catalysts research because of their high intrinsic activity in the hydrochlorination of acetylene.[4-11] Comparing mercuric-free catalysts with supported Pt,[12-13] Pd,[14-16] Ru,[17-19] Cu^{20} and Bi catalysts,[21] promising activity can be achieved with monometallic Au catalysts, the other catalysts suffer from [45] intrinsic defect that active Au^{3+} species being readily reduced to

Au^0 under the reaction conditions and consequently losing its activity, which limit the application of Au catalysts.[22] With the goal of improving the activity and stability of the hydrochlorination of acetylene, some authors modified [50] monometallic Au catalysts by the addition of a second metal.[23-29] For example, Hutchings and coworkers studied the influence of additives, such as Pd, Pt, Ir, Rh, and Ru on Au/AC catalysts, for hydrochlorination of acetylene.[23] Unfortunately, they did not observe a significant increase in activity and selectivity with [55] those metal chlorides added onto Au/AC. Dai and co-workers studied gas-phase hydrochlorination of acetylene over $Au-La^{III}$ and $Au-Co^{III}$ supported on pitch-based spherical activated carbon (SAC).[24-25] The presence of additives of La^{III} and Co^{III} were found to stabilize the catalytic active Au^+ species considerably and [60] inhibit the reduction of Au^{3+} to Au^0 in the preparation process of Au-based/SAC catalysts. Elsewhere, Shen et al. reported the presence of significant synergistic effects on Au-Cu bimetallic catalysts during the hydrochlorination of acetylene.[26] These synergistic effects were mainly from the changes in the electronic [65] structure of the active metal, due to electron-transfer between Au and another metal chloride. Despite these impressive results, most studies have observed that this type of Au-based bimetallic catalyst is not stable enough for practical applications, and

deactivates with time-on-stream. Thus, the development of efficient and robust supported Au-base catalysts with higher stability for the hydrochlorination of acetylene is desirable.

Recently, we have discovered that the use of CsCl as a promoter can facilitate the stabilization of active Au^{3+} species in Au-catalyzed acetylene hydrochlorination.[30] Over $1Au4Cs^I/AC$ catalysts, the maximum conversion of acetylene was 94% and there was only 5% C_2H_2 conversion loss after 50 h running under the reaction conditions of C_2H_2 with an hourly space velocity of 740 h^{-1}. In a more recent report, Dai et al.[31] proposed novel Au-Co(III)-Cu(II) trimetallic structured catalysts, and they assessed them for their ability to promote acetylene hydrochlorination. The long-term stability observed in this work indicates that the ternary Au1Co(III)3Cu(II)1/SAC catalyst can maintain high catalytic activity for at least 6513 h at a low GHSV(C_2H_2) of 30 h^{-1}. This high performance of the ternary Au1Co(III)3Cu(II)1/SAC catalyst was attributed to the synergistic effect of Co(III) and Cu(II) which enhanced the adsorption of hydrogen chloride and increased the amount of Au^+ and Au^{3+} active species over the catalyst. Since highly efficient catalytic systems are always desirable, it is necessary to find new approaches of catalyst promotion. It was reported that the presence of In species in Au-base catalysts can result in the enhancement of activity and selectivity in various reactions.[32-33] This type of modification, typically referred to as the electron-donating effects of In alloying with Au,[26] is highly relevant for many industrial catalysts. In this case, In seems to be a good choice because some of the electron donating from In to Au could significantly enhance the ability of the Au-base catalysts to adsorb hydrogen chloride. The capacity of a catalyst to adsorb hydrogen chloride is associated with its activity and stability for acetylene hydrochlorination. Inspired by the findings in literature mentioned above and as a continuation of our previous work, in this paper, In was selected as the secondary additive to add to the Au-based catalyst. We investigated the effect of the addition of In^{III} to the fully characterized $1Au4Cs^I/AC$ bimetallic catalyst in the hydrochlorination of acetylene. We originally demonstrate that adding a small amount of $InCl_3$ into bimetallic $1AuCs^I/AC$ catalyst is found to be an efficient approach to further improve the catalytic activity and stability of Au-base catalysts for the hydrochlorination of acetylene. These exciting preliminary results are an indication that trimetallic Au-base catalysts represent a highly active and stable catalyst that may replace mercuric chloride.

Experimental

Catalyst preparation

A commercially activated carbon NORIT ROX 0.8 (pellets of 0.8 mm diameter and 5 mm length) was selected for support in the preparation. First, the activated carbon was pretreated with HNO_3 (65 wt.%) at room temperature for 1 h to remove Na, Fe, and Al contaminants. The pre-treated activated carbon was filtered, washed (with deionized water until pH = 7) and then dried at 110 °C for 12 h.

Trimetallic $Au-In^{III}-Cs^I/AC$ catalysts were prepared using impregnation technique. The Au and Cs precursors, $HAuCl_4·4H_2O$ (assay: 48%) and CsCl (99.9 wt.%) powder, were first dissolved in *aqua regia* and the solution was added dropwise to the pre-treated activated carbon support with agitated stirring. After the solution was homogeneously mixed with the support, the system was aged at 40 °C for 4 h, followed by air drying at 110 °C for 12 h. Then, $InCl_3$ (99.9 wt.%) was dissolved in *aqua regia* and the solution was added dropwise to the mixture with agitated stirring. The product was aged, evaporated, and dried at 110 °C in air for 12 h to finally yield the catalysts. Cs loading in all the Cs-containing catalysts was fixed at 4.0 wt.%, Au loading in all the catalysts was fixed at 1.0 wt% at various Au/In^{III} ratios (wt/wt), namely, 1:0.5, 1:1, 1:2 and 1:3, and were denoted as $1Au0.5In^{III}4Cs^I/AC$, $1Au1In^{III}4Cs^I/AC$, $1Au2In^{III}4Cs^I/AC$ and $1Au3In^{III}4Cs^I/AC$, respectively. The same procedure was repeated to prepare the corresponding $1Au/AC$, $4Cs^I/AC$, $1In^{III}/AC$, $1Au1In^{III}/AC$ and $1Au4Cs^I/AC$ catalysts for comparison.

Catalyst characterization

XRD measurements of the catalyst samples were performed on a PANalytical-X'Pert PRO generator with Cu Kα radiation (λ = 0.1541 nm) that was operated at 60 kV and 55 mA. Diffraction patterns were recorded at a scanning rate of 2°min^{-1} and at a step of 0.02°. TEM analysis was conducted using a transmission electron microscope (TEM, Tecnai G2 F30 S-Twin), operating at an acceleration voltage of 300 keV. The solid samples were finely ground. The resultant fine powders were dispersed ultrasonically in the ethanol and then two drops of the solution were transferred to a carbon/Cu grid (Beijing Zhongjingkeyi Technology Co., Ltd.). Grids were allowed to dry before TEM characterization. The sizes of particles on samples were also observed by a transmission electron microscope. The number weighted average Au diameter (d_{TEM}) was determined from a count of 300 particles. The elemental surface composition of the catalysts was controlled by X-ray photoelectron spectroscopy (XPS), acquired with a Kratos AXIS Ultra DLD spectrometer. XPS analysis was performed with the monochromatized aluminum X-ray source and passed energy with an electron analyzer of 40 eV. The pressure in the sample analysis chamber was lower than $6×10^{-9}$ Torr during data acquisition. Binding energies were referred to the C1s line at 284.8 eV. The content of metals within the catalysts was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) with a PerkinElmer Elan DRC-e.

Temperature-programmed desorption (TPD) experiments were performed in a tubular quartz reactor. The samples (about 75 mg) were first treated in situ at 180 °C for 0.5 h using pure C_2H_2 and then cooled to room temperature. The sample was swept with pure Ar at a flow rate of 30 mL min^{-1} for 1 h to remove physisorbed and/or weakly bound species. TPD was performed by heating the sample from room temperature to 500 °C at a ramp rate of 10 °C min^{-1} in pure Ar, and the TPD spectra was recorded by a thermal conductivity detector (TCD). HCl-TPD experiments were performed in the same procedure as the C_2H_2-TPD experiments. Temperature-programmed reduction (TPR) experiments were performed to examine the reducibility of the catalysts on a micro-flow reactor fed with a flow of hydrogen (10% in Ar) at a rate of 45 mL·min^{-1}. The temperature was increased from 30 to 850 °C at a rate of 10 °C·min^{-1}. The hydrogen consumption was measured using a thermal conductivity detector

(TCD). Thermogravimetric analysis (TGA) of the samples was performed using a NETZSCH STA 449C Jupiter instrument coupled to a thermal analyzer in an air atmosphere at a flow rate of 30 mL·min⁻¹. The temperature was increased from 50 to 850 °C at a heating rate of 10 °C·min⁻¹.

Gas phase hydrochlorination of acetylene

Materials

The acetylene (gas, 98.0%) was purified by passing it through a $K_2Cr_2O_7$ solution to get rid of H_2S and PH_3, and a H_2SO_4 solution to get rid of H_2O. The acetylene gas then flowed into the catalyst. All the other gases (HCl and N_2) were of ultra high purity (>99.9%) and were used without further purification.

Catalytic system

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass micro-reactor (i.d. 10 mm). Acetylene (10.0 mL·min⁻¹, 1 bar) and hydrogen chloride (12.0 mL·min⁻¹, 1 bar) were fed though a mixing vessel via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg) with a total GHSV (C_2H_2) of 1480 h⁻¹. The long-term stability experiment was performed in the same apparatus with acetylene (40.5 mL·min⁻¹, 1 bar) and hydrogen chloride (48.6 mL·min⁻¹, 1 bar) fed though a mixing vessel via calibrated mass flow controllers to a heated glass reactor containing the catalyst (1.0 g) with a total GHSV (C_2H_2) of 1200 h⁻¹. A reaction temperature of 180 °C was chosen. Blank tests using an empty reactor filled with quartz wool did not reveal any catalytic activity, and quartz sand was used to extend the bed length, above and below the catalyst itself, separated by quartz wool. The gas phase products were passed through an absorption bottle containing a NaOH solution to remove excess HCl first and then analyzed on-line by GC equipped with a flame ionization detector (FID). Chromatographic separation and identification of the products was carried out using a Porapak N packed column.

Activity and selectivity evaluations

The composition of the reactor outflow (dissolve in the N-methylpyrrolidone solution) was determined using a Waters GCT Premier chromatograph equipped with a HP-5 capillary column. Product mass fractions were obtained using an internal standard. The main product of acetylene hydrochlorination was vinyl chloride, a small amount of the by-products 1,1-dichloroethane and 1,2-dichlorethane were also produced. The gas-phase products of acetylene hydrochlorination were quantified using the peak area normalization method. Given that hydrogen chloride is absorbed by the absorption liquid after the reaction, the volume

of the reaction system can be considered constant during the calculations, and the carbon balance values based on these products are near 100%.The conversion of acetylene and the selectivity to VCM were calculated by Eqs.(1)-(2), as follows:

$$\text{Acetylene conversion (\%)} = \left(1 - \frac{F_A}{F_{A0}}\right) \times 100\% \qquad (1)$$

$$\text{VCM Selectivity (\%)} = \frac{F_{VCM}}{1 - F_A} \times 100\% \qquad (2)$$

Where F_{A0}, F_A, and F_{VCM} represent the volume fraction of acetylene in the raw gas, the volume fraction of remaining acetylene, and the volume fraction of vinyl chloride in the product mixture gas, respectively.

Results and discussion

Additive effect on 1Au4Cs^I/AC for the hydrochlorination of acetylene

First, the additive effect of Co^{II}, La^{III}, In^{III}, or Zn^{II} on 1Au4Cs^I/AC was examined for the hydrochlorination of acetylene to VCM. Table 1 shows the catalytic performances over 1Au4Cs^I/AC catalysts modified with 1 wt.% Co^{II}, La^{III}, In^{III}, and Zn^{II}. In the reaction of acetylene hydrochlorination over 1Au4Cs^I/AC, addition of Co^{II}, La^{III}, or Zn^{II} to the 1Au4Cs^I/AC resulted in much decrease of the activity, which suggests that Co^{II}, La^{III}, or Zn^{II} additives poison the active sites of 1Au4Cs^I/AC, leading to the decrease in activity. In contrast, In^{III}-added 1Au4Cs^I/AC catalysts showed higher conversion when compared with 1Au4Cs^I/AC, which suggests that In^{III} additives have a positive influence on the active sites of 1Au4Cs^I/AC. Furthermore, this catalyst exhibits good stability and the acetylene conversion only decreases slightly under fixed reaction conditions (C_2H_2/HCl = 1:1.2, gas hourly space velocity (GHSV, C_2H_2 based) = 1480 h⁻¹ and reaction temperature = 180 °C) over 12 h, as demonstrated in Table 1. This finding provides a basis for the development of an alternative catalyst for acetylene hydrochlorination. It should be highlighted that the selectivity to VCM was virtually 100% with traces amounts (< 0.1%) of dichlorethane for all Au-base catalysts. Indeed, previous studies reported that the enhancement of the initial activity in the acetylene hydrochlorination reaction using an AuPd alloy NP catalysts, but a significant loss of selectivity can be observed.[8] In this case, considering that the additives can not change, the Au^{3+} species serve as the active center. It is reasonable that in all cases, selectivity to VCM was more than 99.9%, which is consistent with the results reported before.[4-7]

Table 1 Screening of catalyst active components. [a]

Entry	Catalysts	Composition of catalysts [b]	Conv. (%)	Deactivation rate (% h⁻¹) [c]	Sel. (%)
1	1Au4Cs^I/AC	1.0 % Au, 4.0 % Cs^I	88.8	0.35	99.95
2	1Au1Co^{II}4Cs^I/AC	1.0 % Au, 4.0 % Cs^I, 1.0 % Co^{II}	82.7	2.20	99.89
3	1Au1La^{III}4Cs^I/AC	1.0 % Au, 4.0 % Cs^I, 1.0 % La^{III}	81.1	0.63	99.91
4	1Au1In^{III}4Cs^I/AC	1.0 % Au, 4.0 % Cs^I, 1.0 % In^{III}	92.8	0.13	99.93
5	1Au1Zn^{II}4Cs^I/AC	1.0 % Au, 4.0 % Cs^I, 1.0 % Zn^{II}	82.8	1.54	99.72

[a] Reaction conditions: T= 180 °C, V_{HCl}/V_{C2H2} = 1.2, GHSV(C_2H_2) = 1480 h⁻¹.
[b] The catalyst composition is represented by the mass percentage of the active species.
[c] Deactivation rate was defined as (the initial maximum C_2H_2 conversion – the final C_2H_2 conversion)/(deactivation period, h), deactivation period = 12 h.

Hydrochlorination of acetylene by In^{III}-added 1Au4Cs^{I}/AC catalyst

Based on the particularly promising results for the In^{III}-added system, a variation in loading of In^{III} (0.5, 1, 2, and 3 wt.%) on the 1Au4Cs^{I}/AC was performed. Fig. 1 shows the acetylene conversion along with the reaction time of 1Au0.5In^{III}4Cs^{I}/AC, 1Au1In^{III}4Cs^{I}/AC, 1Au2In^{III}4Cs^{I}/AC and 1Au3In^{III}4Cs^{I}/AC catalysts, respectively. The most active 1Au1In^{III}4Cs^{I}/AC catalyst had excellent stability, which was proven by tests. The acetylene conversion of 1Au1In^{III}4Cs^{I}/AC catalyst declines from 92.8% to 89.1% after 50 h running, and the selectivity to VCM maintains at 99.95%, indicating the excellent catalytic performance of 1Au1In^{III}4Cs^{I}/AC catalyst. The catalysts having lower (0.5 wt.%) or higher (2 wt.% and 3 wt.%) indium content show rapid deactivation with respect to the 1Au1In^{III}4Cs^{I}/AC. As suggested by Benitez et al.[34] in a previous study on trimetallic catalysts, this effect could be caused by excessive loading of indium that partially occludes metal particles, limiting reactant accessibility
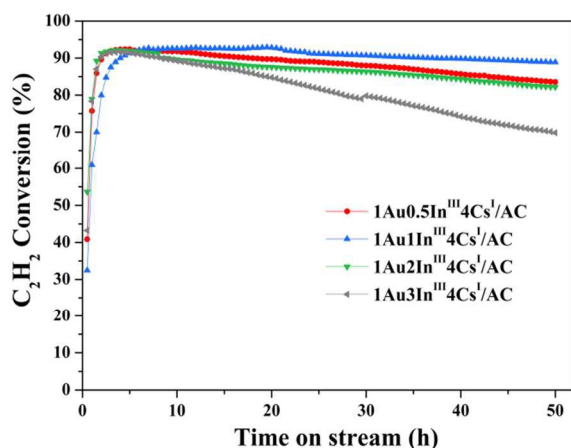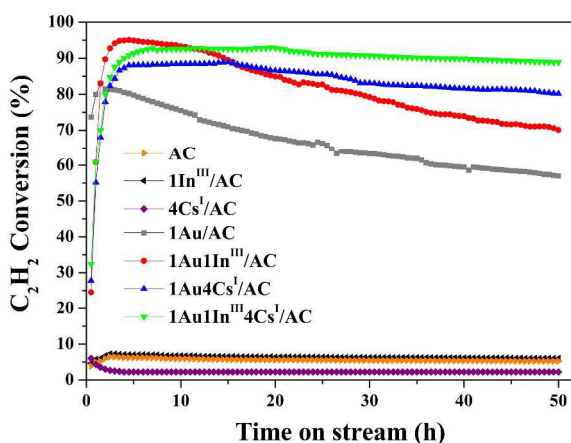
to the active sites. However, considering that four Au-In^{III}-Cs^{I}/AC catalysts present a similar initial activity, thus we speculate that the excessive loading of indium may not occlude metal particles, and we mainly ascribed the detrimental effect of the higher indium content presence to an electronic effect. Thus, based on the results of our catalysis experiments, it is clear that the addition of small amounts of In^{III} to an AC-supported Au-Cs^{I} catalyst, whilst maintaining a constant Au-Cs^{I} ratio, has a positive effect on both activity and stability.

Fig. 2 further compares the acetylene conversion of 1Au/AC, 1In^{III}/AC, 1Au4Cs^{I}/AC, 1Au1In^{III}/AC and 1Au1In^{III}4Cs^{I}/AC catalysts. Only a small amount of VCM is observed in the gas phase over 1In^{III}/AC (<5 % based on C$_2$H$_2$). Controlled tests of the 4Cs^{I}/AC catalyst without Au showed that the maximum acetylene conversion is 5.3%. The activity of the 4Cs^{I}/AC can arise from the presence of trace amounts of metal ions in the carbon matrix which can display some activity to the hydrochlorination reaction of acetylene. Hydrochlorination of acetylene over 1Au/AC catalyst provided high activity with an initial conversion of 82.9%. However, the acetylene conversion of the 1Au/AC catalyst decreases from 82.9% down to 56.7% after running for 50 h, indicating that 1Au/AC is deactivated under reaction conditions. Using the 1Au1In^{III}/AC catalysts, the addition of In^{III} increased the initial activity but this enhancement was lost rapidly. There was a negative effect on the stability observed when the hydrochlorination activity decreases from 95.1% down to 70.9% after running for 50 h. In contrast, the obtained 1Au4Cs^{I}/AC catalyst displays much better stability compared to 1Au/AC catalyst, its acetylene conversion decreases by 8.6% after 50 h running. The catalyst evaluation data in Fig. 2 shows that 1Au1In^{III}4Cs^{I}/AC had the best performance among the tested samples with an initial conversion of 92.8% and stabilized around 89.1%. Therefore, we could conclude that the increasing of activity and stability could be correlated with the addition of In^{III} to the Au-Cs^{I} systems. It is suggested that a synergic effect between In^{III} and Au-Cs^{I} catalytic species exists, which can significantly enhance the catalytic performance of Au-Cs^{I}/AC catalyst for the acetylene hydrochlorination reaction.

Lifetime estimation of the trimetallic 1Au1In^{III}4Cs^{I}/AC catalyst

The important limiting factor for industrial hydrochlorination with supported Au catalyst is the long-term stability under reaction conditions. To further demonstrate the superior performance of Au-Cs^{I}/AC, a gram-scale experiment was carried out using 1.0 g 1Au1In^{III}4Cs^{I}/AC catalyst to investigate the long-term stability of the catalysts for acetylene hydrochlorination reaction. To accelerate the deactivate process of Au-based catalysts, high GHSV (1200 h^{-1}) was carried out. This reaction under GHSV 1200 h^{-1} for 1 h is equivalent to a reaction under GHSV 50 h^{-1} for 24 h.[31] The catalytic results are shown in Fig. 3. As shown, the acetylene conversion of 1Au1In^{III}4Cs^{I}/AC catalyst decreases from 96.3% down to 59.8% after running for 270 h under GHSV 1200 h^{-1}.This indicates that 1Au1In^{III}4Cs^{I}/AC is deactivated under reaction conditions. At this point, the GHSV was adjusted to 50 h^{-1}. This change increases the acetylene conversion to 98.5% within 20 h; at this GHSV, a high conversion is maintained, even after 40 h. This result suggests that the 1Au1In^{III}4Cs^{I}/AC catalyst can maintain high catalytic

activity for at least 6520 h under the upper limit of 50 h^{-1} of industrial hydrochlorination space velocity. Therefore, the present catalytic system is particularly promising in the production of VCM in future application.

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Fig. 3 Lifetime estimate for the 1Au1In^{III}4Cs^{I}/AC catalyst. Reaction conditions: temperature (T) = 180 °C; feed volume ratio V_{HCl}/V_{C2H2} = 1.2.
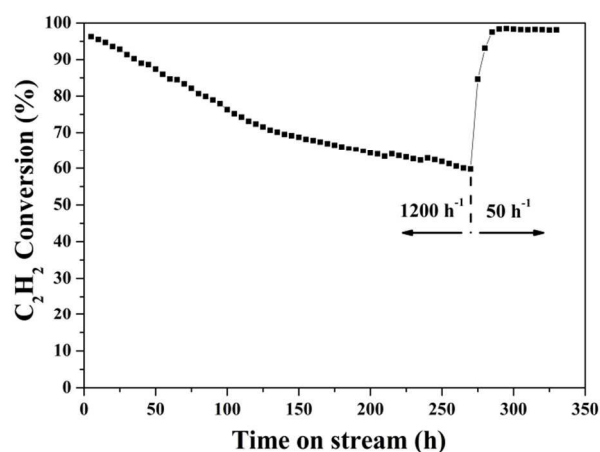
Characterization of In^{III}-added 1Au4Cs^{I}/AC catalyst

Previous literature studies ascribed the activity of the Au-base
10 catalyst to the presence of Au^{3+} species, postulating them to be active sites. In order to obtain a correlation on the activity of VCM production with the amount of Au^{3+} species clusters made on the catalyst surface, samples were tested for acetylene hydrochlorination at different compositions and were carefully
15 analyzed by H$_2$-TPR. Fig. 4 presents the H$_2$-TPR profiles of 4Cs^{I}/AC, 1In^{III}/AC, 1Au/AC, 1Au1In^{III}/AC, 1Au4Cs^{I}/AC and 1Au1In^{III}4Cs^{I}/AC catalysts. For all the catalysts, a distinguishable hydrogen consumption peak in the range of 400-800 °C can be
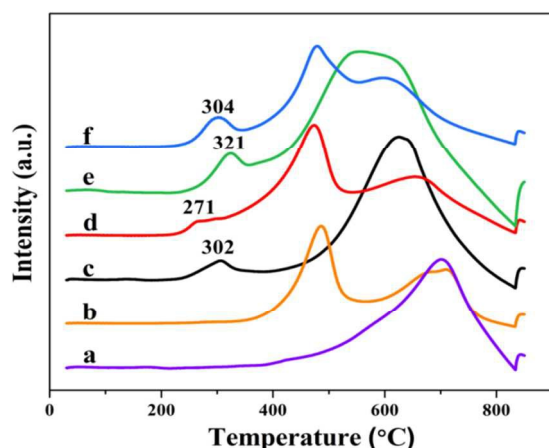

20 **Fig. 4** TPR profiles of fresh catalysts: (a) 4Cs^{I}/AC, (b) 1In^{III}/AC, (c) 1Au/AC, (d) 1Au1In^{III}/AC, (e) 1Au4Cs^{I}/AC and (f) 1Au1In^{III}4Cs^{I}/AC

observed. This peak is a consequence of the reduction of surface groups of activated carbon support.[35-36] For the 4Cs^{I}/AC sample,

it should be noted that the Cs^{I} species can not be reduced by
25 hydrogen (Fig. 4a). For the fresh 1In^{III}/AC catalyst, the TPR profile shows a broad band around 486 °C, which corresponds to the reduction peaks of the In^{III} species (Fig. 4b). In addition, the analysis of 1Au/AC sample led to assign the reduction band around 302 °C to Au^{3+} to Au^{0} (Fig. 4c). The reduction band of
30 Au^{3+} was estimated base on the curve in Fig. 4, which is higher than the result (230-300 °C) reported in Ref.[37] The divergence of results is partly because of the different preparation conditions such as heating rates, as well as different analytical methods. TPR profiles of the fresh 1Au1In^{III}/AC and 1Au4Cs^{I}/AC catalysts
35 disclosed that the InCl$_3$ and CsCl additives greatly affect the reducibility of gold catalysts, a straightforward decrease of temperature in the reduction band of Au^{3+} to 271 °C (Fig. 4d) and a straightforward increase of temperature in the band of Au^{3+} to 321 °C are observed (Fig. 4e), respectively. These shifts indicate
40 strong interactions between Au species and In^{III} or Cs^{I} exist in 1Au1In^{III}/AC or 1Au4Cs^{I}/AC catalysts, respectively. More specifically, the reduction temperature of Au^{3+} may shift to lower or higher temperatures due to the presence of a strong interaction between Au^{3+} and In^{III} or Cs^{I} via the electron transfer which in
45 turn, facilitates or inhibits the reduction. This phenomenon may be attributed to the compound structure formed by Cs^{I} and Au^{3+}leadingto a decrease in the electron density of Au^{3+} during the electron transfer from the Au^{3+} center to the Cs^{I} species, as reported before.[30] In contrast, the In^{III} species act as electron
50 donors and transfer electrons from In atom to the Au^{3+} species to facilitate electron accumulation in the active atom center, resulting in increases in the electron density of Au^{3+}. This direction of electron transfer occurs because In^{III} is less electronegative than Au (Pauling electronegativity: In 1.78, Au
55 2.54). Radnik et al. reported that the modification of the Au/ZnO-I catalyst with In led to a more pronounced Au 4f$_{7/2}$ negative shift of 0.6 eV. They attributed this to the selectivity of the flat facets of the Au nanoparticles (NPs), leaving only atoms at the edges and corners available for detection.[32] Thus, comparing data
60 derived from H$_2$-TPR (Fig. 4) and catalyst testing results (Fig. 2), the poor stability of 1Au1In^{III}/AC catalyst was due to the strong interaction between Au and In atoms via the electron transfer from In to Au. This led to a easier reduction of active Au^{3+} species. In contrast, the presence of Cs^{I} makes reducing Au^{3+}
65 species difficult. Therefore, it is reasonable to conclude that the 1Au4Cs^{I}/AC shows enhanced stability with respect to the reference catalyst 1Au/AC. When In^{III} and Cs^{I} are added to the catalysts simultaneously, the reduction temperature of Au^{3+} shows a negligible shift (2 °C) to a higher temperature as
70 compared to the 1Au/AC sample (Fig. 4f). Such a minor positive shift suggests that there are strong interactions between the three components within the catalyst, and it is reasonable to change the electronic structure of Au. Synergistic effects between Au, Cs^{I} and In^{III} may slightly offset the peak positions of the Au species
75 in the TPR spectra. However, the presence of the Au-In alloy cannot be excluded for the 1Au1In^{III}/AC and 1Au1In^{III}4Cs^{I}/AC catalysts. The alloying of In with Au in the nanosized scale has been reported at room temperature[38]or at a temperature as low as 77 K.[39] The formation of an alloy between Au, In^{III}, and some Cs^{I}
80 species may inhibit the reduction of Au^{3+} and increase the stability of the catalytically active Au^{3+} species. Through

comparing the TCD signals with standard signals, the fractions of different Au species in the fresh catalysts can be estimated. This allows estimations of ca.16.2, 28.1, 46.8 and 39.7% for the 1Au/AC, 1Au1In^{III}/AC, 1Au4Cs^{I}/AC and 1Au1In^{III}4Cs^{I}/AC

catalysts, respectively. It is reasonable to conclude that the addition of Cs^{I} and In^{III} can stabilize the catalytic active Au^{3+} species and inhibit the reduction of Au^{3+} into Au^{0} during the preparation process.

Table 2 Atomic compositions of Au-base catalysts derived from XPS and ICP data, respectively.

Fresh catalysts	Results of XPS			Results of ICP		
	Au (wt.%)	In (%) (wt.%)	Cs (%) (wt.%)	Au (%) (g/Kg)	In (%) (g/Kg)	Cs (%) (g/Kg)
1Au/AC	0.68	/	/	9.76	/	/
1Au4Cs^{I}/AC	0.74	/	3.66	9.64	/	38.26
1Au1In^{III}/AC	0.86	1.14	/	9.82	9.61	/
1Au1In^{III}4Cs^{I}/AC	0.70	1.06	3.84	9.75	9.72	36.42

To check for distinct amounts of Au, In and Cs in the surface and bulk region, XPS and ICP analysis were conducted and the results are summarized in Table 2. Due to the limited escape depth of the photoelectrons, the XPS technique is suitable to study the composition of the material close to the surface. Au content derived from XPS was relatively lower than that from ICP, which meant that Au preferred to anchor in abundant micropores rather than on the surface. In and Cs had similar contents in the two analyses, showing uniform loading in the catalysts. Due to the catalyst preparation procedure, no filtrating of the carbon or catalyst washing was carried out. It is reasonable that the Au, In and Cs metal loading is nearly equal to the nominal amount of metal impregnated onto the support.

TPD is an effective technique providing direct comparison of the adsorption and activation of reactants on different catalysts. Specifically, the desorption temperature in the TPD profiles reflect the binding strength of the adsorbed species with the catalyst surface and the peak area correlates with the amount of active species.[40] Fig. 5 presents the C$_2$H$_2$-TPD profiles for 1In^{III}/AC, 1Au/AC, 4Cs^{I}/AC, 1Au1In^{III}/AC, 1Au4Cs^{I}/AC and 1Au1In^{III}4Cs^{I}/AC catalysts. The first weak desorption peak covers the temperature range of 50-180 °C and corresponds to the acetylene desorption from the support, which is consistent with our previous report.[30] For 1In^{III}/AC (Fig. 5a) and 4Cs^{I}/AC (Fig. 5c), there are negligible acetylene desorption peaks and they can be observed higher than 180 °C, which explains why there is almost no acetylene conversion detected in the reaction. Fig. 5b indicates that there is a considerable amount of acetylene adsorbed on 1Au/AC. The desorption area of acetylene of the bimetallic catalysts 1Au1In^{III}/AC (Fig. 5d) and 1Au4Cs^{I}/AC (Fig. 5e) is larger than that of 1Au/AC catalysts, indicating that addition of
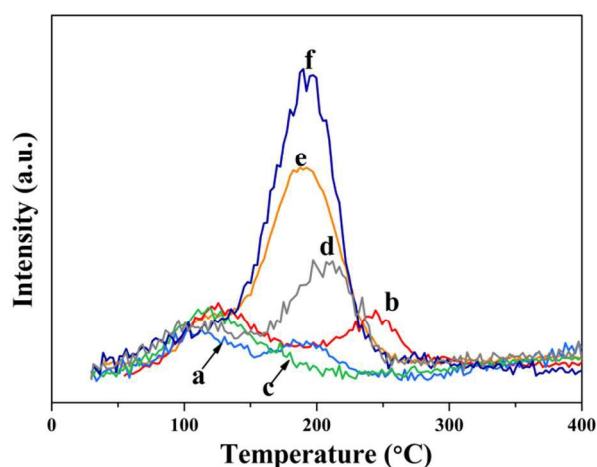

Fig. 5 TPD profiles of acetylene on different samples: (a) 1In^{III}/AC, (b) 1Au/AC, (c) 4Cs^{I}/AC, (d) 1Au1In^{III}/AC, (e) 1Au4Cs^{I}/AC, and (f) 1Au1In^{III}4Cs^{I}/AC.

In^{III} or Cs^{I} improves the catalytic activity of the Au catalyst. Furthermore, the desorption area of acetylene was further increased when In^{III} and Cs^{I} was added to the Au/AC catalysts (Fig. 5f), which is significantly larger than that of either of the bimetallic catalysts. The presence of strong interactions between Au, In^{III} and Cs^{I} is thus confirmed. With respect to the desorption temperature of different Au-base catalysts, as shown in Fig. 5, following order: 1Au/AC > 1Au4Cs^{I}/AC > 1Au1In^{III}/AC > 1Au1In^{III}4Cs^{I}/AC, it is known that the weaker bound state has a lower activation energy for desorption and will therefore undergo desorption at a lower temperature. Thus, the shifts in the higher acetylene desorption peak (1Au/AC) to lower temperatures (1Au1In^{III}4Cs^{I}/AC) may be attributed to the interaction between Au, In^{III} and Cs^{I} in trimetallic catalysts, resulting in different acetylene chemisorption strengths and further catalytic properties.
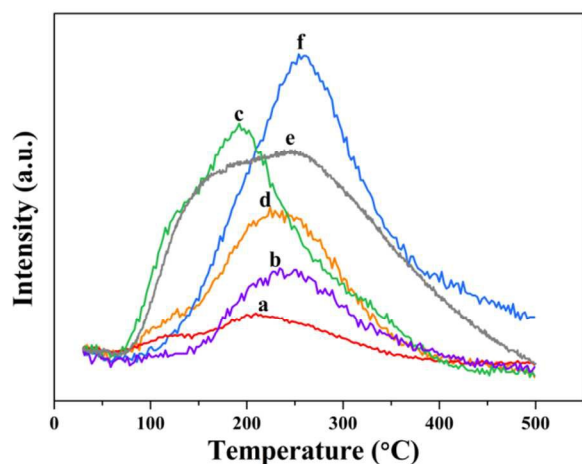
Fig. 6 TPD profiles of hydrogen chloride on different samples: (a) $1In^{III}/AC$, (b) $1Au/AC$, (c) $4Cs^{I}/AC$, (d) $1Au1In^{III}/AC$, (e) $1Au4Cs^{I}/AC$, and (f) $1Au1In^{III}4Cs^{I}/AC$.

HCl-TPD is also used to characterize the active sites for hydrogen chloride adsorption and clarity, the interactions between Au^{3+} and the additives such as CsCl and $InCl_3$, and further determine the contributions of these interactions to the ability of the catalysts to adsorb hydrogen chloride. It is reported in the literature that the capacity of a catalyst to adsorb hydrogen chloride is associated with its activity and stability.[41] As seen in Fig. 6a, 1In/AC shows a weak desorption peak around 200 °C. In the case of 1Au/AC (Fig. 6b), a higher hydrogen chloride desorption at 240 °C is observed, which agrees with the literature, relating to the weakly adsorbed hydrogen chloride. The HCl-TPD profile of the $4Cs^{I}/AC$ catalyst shows three desorption peaks: one at 120 °C and the others at 200 and 300 °C, respectively (Fig. 6c). This indicates that three different adsorbed states of hydrogen chloride exist on the catalyst. The more weakly bound state has a lower activation energy for desorption and will therefore undergo desorption at a lower temperature. This is because of the absence of a desorption peak below 180 °C under the reaction temperature, therefore, only the higher hydrogen chloride desorption peak will be considered. The desorption area of hydrogen chloride for the $4Cs^{I}/AC$ catalyst is significantly larger than 1Au/AC and $1In^{III}/AC$ catalysts. Similarly, the desorption area for hydrogen chloride of the bimetallic catalysts $1Au4Cs^{I}/AC$ (Fig. 6e) is larger than that of $1Au1In^{III}/AC$ catalysts. A relatively sharp peak is observed for $1Au4Cs^{I}/AC$ catalyst at 250 °C. The $1Au4Cs^{I}/AC$ catalyst also exhibits a peak at 250 °C but with a more pronounced tail than the $1Au1In^{III}/AC$ catalyst, which continues up to approximately 500 °C. Such tails indicate continuous desorption of hydrogen chloride during TPD analysis. The desorption area of hydrogen chloride for the $1Au1In^{III}4Cs^{I}/AC$ (Fig. 6f) trimetallic catalyst is significantly larger than that of either of the bimetallic catalysts and the monometallic catalysts. This favorable adsorption of hydrogen chloride on $1Au1In^{III}4Cs^{I}/AC$ can be explained by the electron transfer from In atoms to Au species, confirmed by H_2-TPR, which enhanced

the electron-donating ability of Au and allowed the catalyst to combine with more hydrogen chloride. Thus, it is clear that the addition of In^{III} can enhance the adsorption of hydrogen chloride and activate acetylene, and hence the hydrochlorination of acetylene.
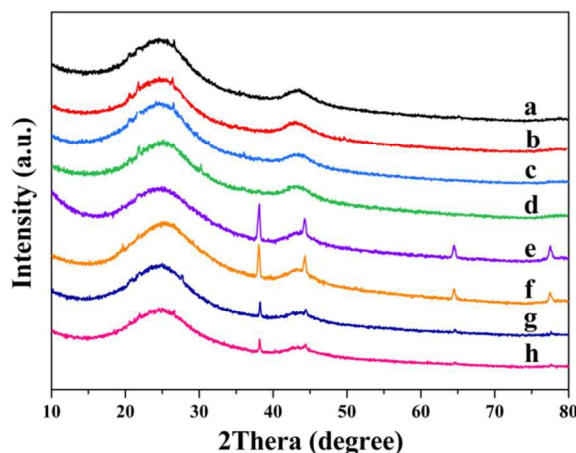

Fig. 7 XRD patterns of: (a) fresh 1Au/AC, (b) fresh $1Au1In^{III}/AC$, (c) fresh $1Au4Cs^{I}/AC$, (d) fresh $1Au1In^{III}4Cs^{I}/AC$, (e) used 1Au/AC, (f) used $1Au1In^{III}/AC$, (g) used $1Au4Cs^{I}/AC$, and (h) used $1Au1In^{III}4Cs^{I}/AC$.

Fig. 7 displays the XRD patterns of the fresh and used 1Au/AC, $1Au4Cs^{I}/AC$, $1Au1In^{III}/AC$, and $1Au1In^{III}4Cs^{I}/AC$ as a representative of the $Au-In^{III}-Cs^{I}/AC$ trimetallic catalyst. The peak around 2θ of 26° corresponds to (002) planes of graphitized carbon from AC. Apart from the amorphous diffraction peaks of the AC, no discernible Au^0 reflection is detected in fresh Au-base catalysts. This is indicative of extremely small Au-containing NPs on the AC surface below the detection limit of this technique (smaller than 4 nm) or most of the Au exists as non-crystalline Au^{3+} species. However, in the case of used 1Au/AC and $1Au1In^{III}/AC$ catalysts, it shows diffraction peaks located at 2θ values of 38.12°, 44.34°, and 64.54° which are assigned to Au (111), Au (200), and Au (220) planes, respectively. In contrast, for $1Au4Cs^{I}/AC$ and $1Au1In^{III}4Cs^{I}/AC$ catalysts, the two broad diffraction peaks are marginally differentiable from the background, as shown at 38.12° and 44.34°, and were observed after the sample was tested for this reaction of 50 h, indicating the smallest fraction of Au^{3+} reduction to Au^0 or the smallest amount of catalyst sintering. This sintering tendency is reflected in the activity data in Fig. 2 that Au^{3+} is reduced into Au^0, contributing to the deactivation of the Au catalyst. These findings confirm that metal additives cannot completely inhibit the sintering of the Au catalyst during the hydrochlorination reaction but are able to obstruct the reduction of the active component to some extent. This phenomenon was previously observed by Dai et al.[24-25]

The TEM of fresh and used 1Au/AC, $1Au1In^{III}/AC$, $1Au4Cs^{I}/AC$, and $1Au1In^{III}4Cs^{I}/AC$ catalysts was performed to further evaluate possible sintering of NPs after the reaction. Fig. 8 shows exemplary TEM images of selected Au-base catalysts. As
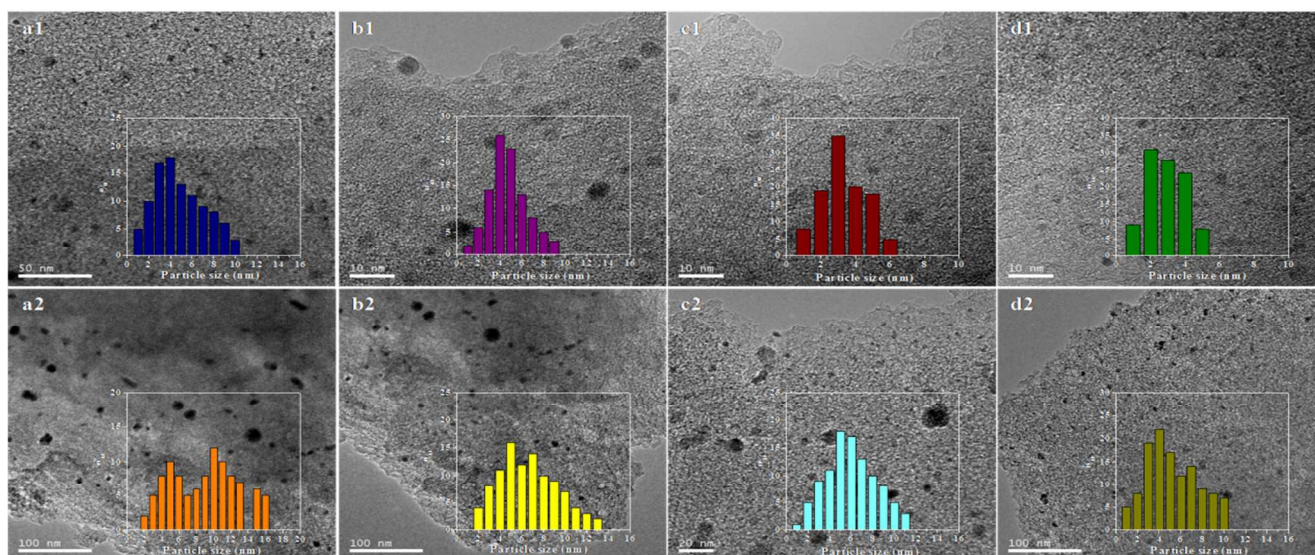
Fig. 8 Representative TEM figures of (1) fresh and (2) used 1Au/AC (a), 1Au1In^{III}/AC (b), 1Au4Cs^{I}/AC (c), and 1Au1In^{III}4Cs^{I}/AC (d), respectively.
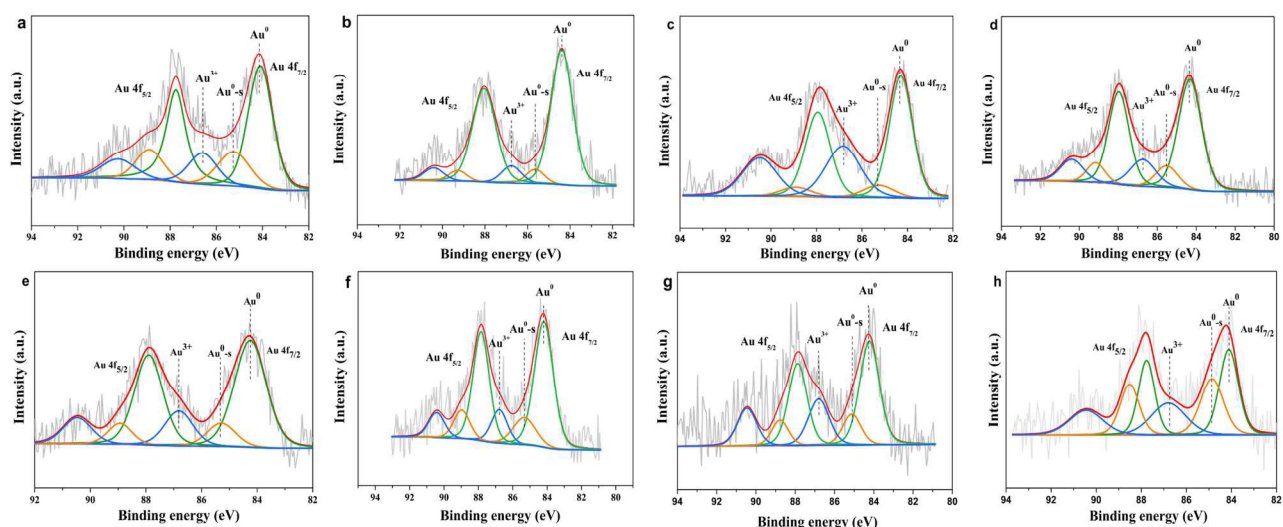

5 **Fig. 9** XPS spectrum and simulation for the samples: (a) fresh 1Au/AC catalyst, (b) used 1Au/AC catalyst, (c) fresh 1Au4Cs^{I}/AC catalyst, (d) used 1Au4Cs^{I}/AC catalyst, (e) fresh 1Au1In^{III}/AC catalyst, (f) used 1Au1In^{III}/AC catalyst, (g) fresh 1Au1In^{III}4Cs^{I}/AC catalyst, (h) used 1Au1In^{III}4Cs^{I}/AC catalyst.

can be seen, the fresh 1Au/AC (Fig. 8a1) and 1Au1In^{III}/AC (Fig. 8b1) catalysts are made up of small metal NPs ranging from 1 to 10 nm in diameter. For the samples 1Au4Cs^{I}/AC (Fig. 8c1) and 1Au1In^{III}4Cs^{I}/AC (Fig. 8d1), the NPs are made up of small metal particles ranging from 1 to 6 nm in diameter, indicating the particles are highly dispersed. However, monometallic Au/AC catalysts are not resistant to sintering and show a large particle 15 size distribution ranging from 2 to 16 nm in diameter after reaction for 50 h (Fig. 8a2). This indicates that the size of distribution for Au NPs in this sample is quite heterogeneous and that the agglomeration of Au occurs easily. The similar phenomenon also has been observed over 1Au1In^{III}/AC sample 20 (Fig. 8b2). For the sample using 1Au4Cs^{I}/AC (Fig. 8c2) and

1Au1In^{III}4Cs^{I}/AC (Fig. 8d2), all particles imaged in the catalysts had diameters of about 1-11 nm. This is indicative of the addition of Cs^{I} to the catalysts, so it can effectively inhibit the catalyst sintering during the hydrochlorination reaction, in accordance 25 with the XRD results (Fig. 7). It is important to note that the addition of additives can not inhibit the sintering of the Au catalyst in the reaction process, but can obstruct the reduction of active components to a certain extent, as previously stated.[23-24] It is well known that the particle size of the active metal component 30 of the catalyst has an important influence on the catalytic performance. For the hydrochlorination reaction of acetylene, catalytic activity was correlated with Au content and the number of active sites for the adsorption of HCl and C_2H_2 (i.e., the

dispersion of Au). This is because the activity was ascribed to Au^{3+} species at the perimeter of the Au NPs in contact with the support.[36] Thus, high conversions required high Au dispersion. $1Au1In^{III}4Cs^{I}/AC$ had a stable conversion without significant Au agglomeration formation after 50 h test, revealing the valuable improvement of Au dispersion after the introduction of In^{III} and Cs^{I} in 1Au/AC.

Table 3 Quantification and identification from XPS of Au species over Au-base catalysts.

Catalysts	Au species (%)			Binding energies (eV)		
	Au^{3+}	Au^0	Au^0-s	Au^{3+}	Au^0	Au^0-s
1Au/AC fresh	17.8	60.3	21.9	86.6	84.2	85.2
1Au/AC used	9.8	82.9	7.3	86.8	84.4	85.6
$1Au4Cs^{I}/AC$ fresh	35.8	56.2	8.0	86.7	84.3	85.4
$1Au4Cs^{I}/AC$ used	21.7	55.3	18.4	87.2	84.3	85.3
$1Au1In^{III}/AC$ fresh	20.5	66.5	13.0	86.8	84.2	85.3
$1Au1In^{III}/AC$ used	15.2	67.4	17.4	86.8	84.2	85.3
$1Au1In^{III}4Cs^{I}/AC$ fresh	27.0	57.1	15.9	86.8	84.2	85.1
$1Au1In^{III}4Cs^{I}/AC$ used	24.6	51.3	24.1	86.7	84.2	85.2

Au^{3+} species in the NPs deposited over the carbon support is the active sites for hydrochlorination reaction of acetylene,[37, 41-42] therefore, the reduction of Au^{3+} to metallic Au^0 is the predominant reason for the rapid deactivation of the Au-base catalysts. In order to provide evidence for this viewpoint, we carried out XPS to demonstrate the valence state changes of the catalyst structure before and after the reaction. It should be noted that more than one Au species was evident, so curve fitting was employed to determine the ratio of each species, as shown in Fig. 9. Due to the reduction property of carbon towards Au^{3+}, there is a large number of Au^0 in fresh Au-base catalysts. It should also be noted that some small metallic gold clusters (Au^0-s) are also formed in the fresh Au-base catalyst, which coincided with the previous publications.[6] However, the Au^0-s species are inactive and not involved in the reaction. In fresh 1Au/AC, $1Au4Cs^{I}/AC$, $1Au1In^{III}/AC$ and $1Au1In^{III}4Cs^{I}/AC$ samples, the relative content of Au^{3+} is 17.8%, 35.8%, 20.5% and 27.0%, respectively (Table 3). There is a higher content of Au^{3+} in $1Au1In^{III}/AC$, $1Au4Cs^{I}/AC$ and $1Au1In^{III}4Cs^{I}/AC$ also illustrating that the existence of In^{III} and/or Cs^{I} species inhibits the reduction of Au^{3+} into Au^0 in the preparation process. The result from the previous study revealed,[14] the optimal Au^{3+} amount would be about ca. 30 % and excess amounts will not further increase the activity. This was explained by the existence of active sites at the Au/C interface, and not just by the presence of Au^{3+} species on top of Au nanoparticles.[14-15] Under the reaction conditions, Au^{3+} is reduced into Au^0, contributing to the deactivation of the Au catalyst. Only 9.8% of Au^{3+} species presented after the reaction using 1Au/AC catalysts, demonstrating that a reduction and/or agglomeration of Au^{3+} species occurs in the reaction process. This is supported by the XRD and TEM analyses. In contrary, there is a considerable amount of Au^{3+} in the used $1Au1In^{III}/AC$ (15.2%) and $1Au4Cs^{I}/AC$ (21.7%) catalysts (Table 3), indicating that the incorporation of the Cs^{I} and In^{III} helps to keep the active Au^{3+} species stable at high temperature under reducing atmosphere. In addition, when using the $1Au1In^{III}4Cs^{I}/AC$

catalyst, there are still large amounts of Au^{3+} (24.6%). These results indicate that the stabilization of Au^{3+} species was almost certainly a result of the addition of Cs^{I} and In^{III}, where the configuration of the Cs^{I} around the Au^{3+} species inhibits the reduction of Au^{3+} to Au^0, while the inhibiting effect of In^{III} on Au^{3+} reduction may by further stabilize the high oxidation state of Au^{3+}. This was through electron transfer and strengthening the adsorption of hydrogen chloride to the electron-rich catalyst in the reaction process. In combination with the catalytic performances of these catalysts (Fig. 2), it is reasonable to conclude that a high content of Au^{3+} leads to the best catalytic performance, as displayed by the $1Au1In^{III}4Cs^{I}/AC$.

Table 4 Textural properties of Textural properties of the activated carbon supports and the prepared Au-base catalysts.

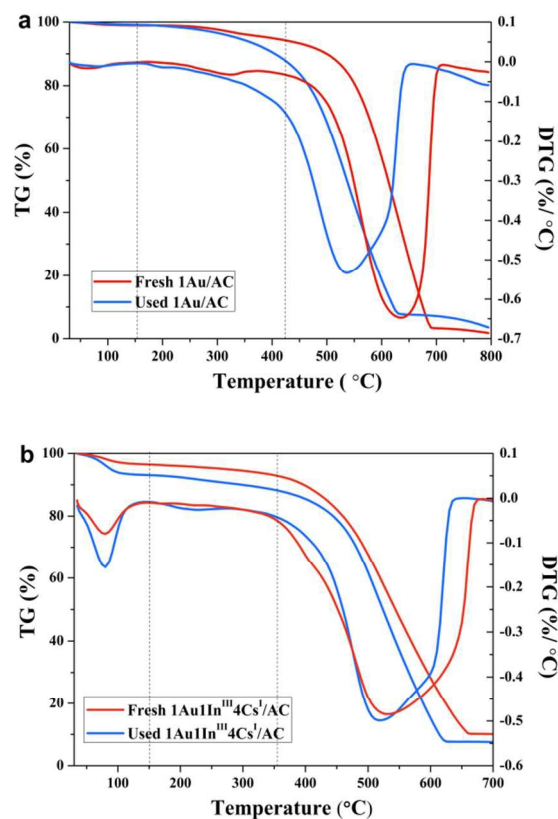| Sample	S_{BET} (m^2 g^{-1})		Total pore volume (cm^3 g^{-1})	
	Fresh	Used	Fresh	Used
AC	1162	/	0.63	/
1Au/AC	1128	839	0.58	0.46
1Au4CsI/AC	966	925	0.53	0.52
1Au1InIII/AC	1087	986	0.62	0.58
1Au1InIII4CsI/AC	868	853	0.49	0.48

Fig. 10 TGA curves of fresh and used (a) 1Au/AC and (b) $1Au1In^{III}4Cs^{I}/AC$ catalysts.

Table 5 Coke deposition on the Au-base catalysts.

Catalyst	Amount of carbon deposition (%)
1Au/AC	5.5
1Au1In^{III}/AC	4.5
1Au4Cs^I/AC	1.7
1Au1In^{III}4Cs^I/AC	2.2

Au^{3+} is reduced to Au^0 during the reaction, however, carbon deposition may also result in pore clogging of the support and covering some parts of the active sites and decreasing the catalyst activity. Thus, to provide direct evidence of coke deposition, BET and TGA experiments were performed. Table 4 shows the textural parameters of the supports and the prepared Au-base catalysts. As we can see, the BET surface areas of the Au-base catalysts are in the range of 860-1130 m$^2 \cdot$g^{-1}, which have a small decrease compared with that of blank AC support. This result may be caused by the phenomenon called the dilution effect, in which the loading of the active component decreases the ratio of the carriers in the catalysts.[25] The proportion of the carriers is reduced with a rise of the active component loading, and the dilution effect becomes more significant. After the reaction, the BET surface area of the 1Au/AC catalyst reduces to 839 m^2 g^{-1} (ΔS_{BET}%=25.6%), which may be caused by the carbon deposition. The addition of Cs^I and/or In^{III} into the Au catalyst results in a change in the variation amplitude of the catalyst's BET surface areas, following the order: 1Au1In^{III}/AC (9.3%) > 1Au4Cs^I/AC (4.3%) > 1Au1In^{III}4Cs^I/AC (1.8%). Therefore, the optimal 1Au1In^{III}4Cs^I/AC catalyst may have the least carbon deposition.

The amount of carbon deposition on the catalysts was determined based on the calculation method described before.[24-25] The activated carbon can react with oxygen to release CO and CO$_2$, contributing to the weight and loss of support. Thus, in order to eliminate the effect mentioned above, the amount of carbon deposition should be equal to the difference of the weight loss between the fresh and used catalysts in the temperature range of coke burning.[24-25, 43-44] Fig. 10 shows the TG and DTG curves of the fresh and used 1Au/AC (Fig. 10a) and 1Au1In^{III}4Cs^I/AC (Fig. 10b) catalysts. It can be seen that neither the fresh nor the used catalyst has a visible loss of mass before 150 °C, indicating that minor water adsorption on the catalysts surface occurs. The fresh 1Au1In^{III}4Cs^I/AC catalyst (Fig. 10b) shows a slow loss of weight within the range 150-458 °C. When the temperature exceeds 458 °C, the catalyst undergoes rapid weight loss, which is mainly due to the combustion of activated carbon. Table 5 lists the amount of coke formed during the reaction obtained by comparing the differences between the fresh and used catalysts in the special temperature range reflecting the coke deposition after a reaction time of 50 h. As shown, the amount of coke deposited on the 1Au/AC catalyst is highest, at 5.5%. The amount of coke deposition is significantly reduced after addition of Cs^I, indicating that addition of Cs^I can effectively reduce the amount of coke deposition on Au catalysts. In contrast, In^{III} addition has a negligible effect, reducing the amount of coke deposited during the reaction when it is present in small amounts. The amount of carbon deposition on the catalysts shows the trend 1Au4Cs^I/AC (1.7%) < 1Au1In^{III}4Cs^I/AC (2.2%) < 1Au1In^{III}/AC (4.5%) < 1Au/AC (5.5%). The positive effect of Cs^I addition on the inhibition of coke deposition is thus confirmed.

Conclusion

In summary, we have shown that the addition of In^{III} as a third metallic component to AC supported 1Au4Cs^I catalyst affects the activity and stability in the hydrochlorination of acetylene. The enhancement of stability observed for Au/In^{III}/Cs^I weight ratio of 1:1:4 which delivered a stable performance with the conversion of acetylene reaching more than 92.8% and there was only 3.7% C$_2$H$_2$ conversion loss after 50 h running under the reaction conditions is particularly remarkable. Moreover, the 1Au1In^{III}4Cs^I/AC catalyst delivered a stable performance with an estimated lifetime exceeding 6520 h at C$_2$H$_2$ hourly space velocity 50 h^{-1}. It was indicated that the addition of In^{III} increased the electron density of Au^{3+} species via electron transfer from In atoms to Au^{3+} center can increase the adsorption of hydrogen chloride and inhibit the reduction of Au^{3+} to Au^0 during acetylene hydrochlorination and hence improve the catalytic stability. This study shows that the addition of minor additional In^{III} components to bimetallic 1Au4Cs^I/AC catalysts results in a synergistic effect to enhance the activity and the stability of Au-based catalysts. The excellent catalytic performance of the 1Au1In^{III}4Cs^I/AC catalyst demonstrated its potential as an alternative to mercury chloride catalysts for acetylene hydrochlorination. Lastly, the efforts to further reduce the Au loading will be made and reported in future work.

Acknowledgements

Notes and references

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1 M.W. Allsopp, G. Vianello, In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2000.

2 G.J.Hutchings, D.T. Grady, Hydrochlorination of acetylene: The effect of mercuric chloride concentration on catalyst life, Appl. Catal. 1985, 17, 155-160.

3 G.J.Hutchings, Vapor phase hydrochlorination of acetylene: Correlation of catalytic activity of supported metal chloride catalysts, J. Catal. 1985, 96, 292-295.

4 B. Nkosi, N.J. Coville, G.J. Hutchings, Reactivation of a supported gold catalyst for acetylene hydrochlorination, J. Chem. Soc., Chem. Commun. 1988, 1, 71-72.

5 M. Conte, A.F. Carley, C. Heirene, D.J. Willock, P. Johnston, A.A. Herzing, et al., Hydrochlorination of acetylene using a supported gold catalyst: A study of the reaction mechanism, J. Catal. 2007, 250, 231-239.

6 M. Conte, C.J. Davies, D.J. Morgan, A.F. Carley, P. Johnston, G.J. Hutchings, Characterization of Au^{3+} species in Au/C catalysts for the hydrochlorination reaction of acetylene, Catal. Lett. 2014, 144, 1-8.

7 M. Conte, C.J. Davies, D.J. Morgan, T.E. Davies, A.F. Carley, P. Johnston, et al., Modifications of the metal and support during the

deactivation and regeneration of Au/C catalysts for the hydrochlorination of acetylene, Catal. Sci. Technol. 2013, 3, 128-134.

8   M. Conte, A.F. Carley, G. Attard, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Hydrochlorination of acetylene using supported bimetallic Au-based catalysts, J. Catal. 2008, 257, 190-198.

9   W. Wittanadecha, N. Laosiripojana, A. Ketcong, N. Ningnuek, P. Praserthdam, J.R. Monnier, et al., Preparation of Au/C catalysts using microwave-assisted and ultrasonic-assisted methods for acetylene hydrochlorination, Appl. Catal. A: Gen. 2014, 475, 292-296.

10 W. Wittanadecha, N. Laosiripojana, A. Ketcong, N. Ningnuek, P. Praserthdam, J.R. Monnier, et al., Development of Au/C catalysts by the microwave-assisted method for the selective hydrochlorination of acetylene, React. Kinet. Mech. Catal. 2014, 112, 189-198.

11 X. Yang, C. Jiang, Z. Yang, J. Zhang, Hydrochlorination of acetylene using SiC foam supported structured C/Au catalysts, J. Mater. Sci Technol. 2014, 30, 434-440.

12 S.A. Mitchenko, T.V. Krasnyakova, R.S. Mitchenko, A.N. Korduban, Acetylene catalytic hydrochlorination over powder catalyst prepared by pre-milling of K_2PtCl_4 salt, J. Mol. Catal A: Chem. 2007, 275, 101-108.

13 S.A. Mitchenko, E.V. Khomutov, A.A. Shubin, Y.M. Shul'ga, Catalytic hydrochlorination of acetylene by gaseous HCl on the surface of mechanically pre-activated K_2PtCl_6 salt, J. Mol. Catal. A: Chem. 2004, 212, 345-352.

14 S.A. Mitchenko, T.V. Krasnyakova, I.V. Zhikharev, Effect of mechanicochemical treatment on the activity of K_2PdCl_4 in the heterogeneous catalytic hydrochlorination of acetylene, Theor. Exp. Chem. 2010, 46, 32-38.

15 T.V. Krasnyakova, I.V. Zhikharev, R.S. Mitchenko, V.I. Burkhovetski, A.M. Korduban, T.V. Kryshchuk, et al., Acetylene catalytic hydrochlorination over mechanically pre-activated K_2PdCl_4 salt: A study of the reaction mechanism, J. Catal. 2012, 288, 33-43.

16 F. Wang, L. Wang, J. Wang, Y. Zhao, Y. Wang, D. Yang, Bimetallic Pd-K/Y-zeolite catalyst in acetylene hydrochlorination for PVC production, React. Kinet. Mech. Catal. 2015, 114, 725-734.

17 Y. Pu, J. Zhang, L. Yu, Y. Jin, W. Li, Active ruthenium species in acetylene hydrochlorination, Appl. Catal. A: Gen. 2014, 488, 28-36.

18 J. Zhang, W. Sheng, C. Guo, W. Li, Acetylene hydrochlorination over bimetallic Ru-based catalysts, RSC Adv. 2013, 3, 21062-21068.

19 G. Li, W. Li, H. Zhang, Y. Pu, M. Sun, J. Zhang, Non-mercury catalytic acetylene hydrochlorination over Ru catalysts enhanced by carbon nanotubes, RSC Adv. 2015, 5, 9002-9008.

20 K. Zhou, J. Si, J. Jia, J. Huang, J. Zhou, G. Luo, et al., Reactivity enhancement of N-CNTs in green catalysis of C_2H_2 hydrochlorination by a Cu catalyst, RSC Adv. 2014, 4, 7766-7769.

21 K. Zhou, J. Jia, X. Li, X. Pang, C. Li, J. Zhou, et al., Continuous vinyl chloride monomer production by acetylene hydrochlorination on Hg-free bismuth catalyst: From lab-scale catalyst characterization, catalytic evaluation to a pilot-scale trial by circulating regeneration in coupled fluidized beds, Fuel Process Technol. 2013, 108, 12-18.

22 B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, F.E. Wagner, Hydrochlorination of acetylene using gold catalysts: a study of catalyst deactivation, J. Catal. 1991, 128, 366-377.

23 M. Conte, A.F. Carley, G. Attard, A.A. Herzing, C.J. Kiely, G.J. Hutchings, Hydrochlorination of acetylene using supported bimetallic Au-based catalysts, J. Catal. 2008, 257, 190-198.

24 H. Zhang, B. Dai, X. Wang, L. Xu, M. Zhu, Hydrochlorination of acetylene to vinyl chloride monomer over bimetallic Au-La/SAC catalysts, J. Ind. Eng. Chem. 2012, 18, 49-54.

25 H. Zhang, B. Dai, X. Wang, W. Li, Y. Han, J. Gu, et al., Non-mercury catalytic acetylene hydrochlorination over bimetallic Au-Co(III)/SAC catalysts for vinyl chloride monomer production, Green Chem. 2013, 15, 829-836.

26 S. Wang, B. Shen, Q. Song, Kinetics of acetylene hydrochlorination over bimetallic Au-Cu/C catalyst, Catal. Lett. 2010, 134, 102-109.

27 K. Zhou, W. Wang, Z. Zhao, G. Luo, J.T. Miller, M.S. Wong, et al., Synergistic Gold-Bismuth catalysis for non-mercury hydrochlorination of acetylene to vinyl chloride monomer, ACS Catal. 2014, 4, 3112-3116.

28 Y. Pu, J. Zhang, X. Wang, H. Zhang, L. Yu, Y. Dong, et al., Bimetallic Au-Ni/CSs catalysts for acetylene hydrochlorination, Catal. Sci. Technol. 2014, 4, 4426-4432.

29 H. Zhang, W. Li, X. Li, W. Zhao, J. Gu, X. Qi, et al., Non-mercury catalytic acetylene hydrochlorination over bimetallic Au-Ba(II)/AC catalysts, Catal. Sci. Technol. 2015, 5, 1870-1877.

30 J. Zhao, J. Xu, J. Xu, J. Ni, T. Zhang, X. Xu, et al., Activated-carbon-supported Gold-Cesium(I) as highly effective catalysts for hydrochlorination of acetylene to vinyl chloride, ChemPlusChem. 2015, 80, 196-201.

31 H. Zhang, B. Dai, W. Li, X. Wang, J. Zhang, M. Zhu, et al., Non-mercury catalytic acetylene hydrochlorination over spherical activated-carbon-supported Au-Co(III)-Cu(II) catalysts, J. Catal. 2014, 316, 141-148.

32 J. Radnik, C. Mohr, P. Claus, On the origin of binding energy shifts of core levels of supported gold nanoparticles and dependence of pretreatment and material synthesis, Phys. Chem. Chem. Phys. 2003, 5, 172-177.

33 Q.Y. Yang, Y. Zhu, L. Tian, S.-H. Xie, Y. Pei, H. Li, et al., Preparation and characterization of Au-In/APTMS-SBA-15 catalysts for chemoselective hydrogenation of crotonaldehyde to crotyl alcohol, Appl. Catal. A: Gen. 2009, 369, 67-76.

34 V.M. Benitez, C.L. Pieck, Influence of Indium Content on the Properties of Pt-Re/Al$_2$O$_3$ Naphtha Reforming Catalysts, Catal. Lett. 2010, 136, 45-51.

35 S.R. de Miguel, O.A. Scelza, M.C. Roman-Martinez, C. Salinas-Martinez de Lecea, D. Cazorla-Amoros, A. Linares-Solano, States of Pt in Pt/C catalyst precursors after impregnation, drying and reduction steps, Appl. Catal. A: Gen.1998, 170, 93-103.

36 J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbons, Carbon. 1999, 37, 1379-1389.

37 M. Conte, C.J. Davies, D.J. Morgan, T.E. Davies, D.J. Elias, A.F. Carley, et al., Aqua regia activated Au/C catalysts for the hydrochlorination of acetylene, J. Catal. 2013, 297, 128-136.

38 H.G. Boyen, A. Ethirajan, G. Kastle, F. Weigl, P. Ziemann, G. Schmid, et al., Alloy formation of supported gold nanoparticles at their transition from clusters to solids: Does size matter?, Phys. Rev. Lett. 2005, 94, 016801-016804.

39 H.G. Boyen, G. Indlekofer, G. Gantner, H. Stupp, A. Cossy-Favre, P. Oelhafen, Intermixing at Au-In interfaces as studied by photoelectron spectroscopy, Phys. Rev. B: Condens. Matter. 1995, 51, 17096-17099.

40 X. Li, X. Pan, L. Yu, P. Ren, X. Wu, L. Sun, et al., Silicon carbide-derived carbon nanocomposite as a substitute for mercury in the catalytic hydrochlorination of acetylene, Nat. Commun. 2014, 5, 3688.

41 J. Zhang, Z. He, W. Li, Y. Han, Deactivation mechanism of AuCl$_3$ catalyst in acetylene hydrochlorination reaction: a DFT study, RSC Adv. 2012, 2, 4814-4821.

42 X. Li, M. Zhu, B. Dai, AuCl$_3$ on polypyrrole-modified carbon nanotubes as acetylene hydrochlorination catalysts, Appl. Catal. B: Environ. 2013, 142-143, 234-240.

43 K. Dumbuya, G. Cabailh, R. Lazzari, J. Jupille, L. Ringel, M. Pistor, et al., Evidence for an active oxygen species on Au/TiO$_2$(110) model catalysts during investigation with in situ X-ray photoelectron spectroscopy, Catal. Today. 2012, 181, 20-25.

44 D. He, X. Jiao, P. Jiang, J. Wang, B. Q. Xu, An exceptionally active and selective Pt-Au/TiO$_2$ catalyst for hydrogenation of the nitro group in chloronitrobenzene, Green Chem. 2012, 14, 111-116.