# Activated-Carbon-Supported Gold–Cesium(I) as Highly Effective Catalysts for Hydrochlorination of Acetylene to Vinyl Chloride

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The synthesis of vinyl chloride from acetylene by hydrochlorination has gained tremendous interest in coal-based chemistry. Bimetallic gold-cesium(I)/activated carbon (Au–Cs<sup>I</sup>/AC) catalysts were found to have a higher catalytic activity and stability for acetylene hydrochlorination when compared with gold catalysts. Over  $1 \text{Au}-4 \text{Cs}^{I}/\text{AC}$  catalysts, the maximum conversion of acetylene was 94% and there was only 5% C<sub>2</sub>H<sub>2</sub> conversion loss after 50 h of running time. Moreover, the  $1 \text{Au}-4 \text{Cs}^{I}/\text{AC}$ catalyst delivered a stable performance during a 500 h test

# Introduction

Vinyl chloride monomer (VCM) is an important chemical material and intermediate commonly used in the production of polyvinyl chloride (PVC).<sup>[1]</sup> Acetylene hydrochlorination is an important coal-based route for the industrial production of VCM following the reaction  $C_2H_2 + HCI \rightarrow CH_2 = CHCI$  ( $\triangle H =$  $-124.8 \text{ kJ mol}^{-1}$ .<sup>[2]</sup> One of the advantages of using this route is related to its economic benefit compared with the oxychlorination reaction based on petroleum. In addition, the energy structure of China, with huge coal reserves, also means that acetylene hydrochlorination is a very in-demand reaction; however, it is restricted by the toxicity and volatility of mercury chloride used as a common catalyst for industrial acetylene hydrochlorination.<sup>[3]</sup> Therefore, extensive efforts have been made to explore non-mercury catalysts as alternatives for acetylene hydrochlorination.<sup>[4]</sup> The pioneering study by Hutchings and co-workers revealed that gold in the Au<sup>3+</sup> state demonstrated unique catalysis in the gas-phase hydrochlorination of acetylene to form vinyl chloride.<sup>[2a,4a,c,5]</sup> Subsequently, AuCl<sub>3</sub> species supported on different carbon materials were demonstrated to be the most active catalyst for the hydrochlorination of acetylene.<sup>[6]</sup> Despite these impressive results, the high standard electrode potential of Au<sup>3+</sup> may result in active species being readily reduced to Au<sup>0</sup> under the reaction conditions, and consequently, losing activity.<sup>[2a,7]</sup> Therefore, extensive efforts have to be made to improve the stability of AuCl<sub>3</sub> catalysts for acetylene hydrochlorination.

The design of catalysts has, so far, been the main tool employed to attain the required level of catalytic performance for with the conversion of acetylene and the selectivity of vinyl chloride reaching more than 99.8 and 99.9%, respectively. Temperature-programmed reduction of H<sub>2</sub>, temperature-programmed desorption of C<sub>2</sub>H<sub>2</sub>, and X-ray photoelectron spectroscopy techniques were further applied to detect structural information on the Au–Cs<sup>I</sup>/AC catalysts. Additives of CsCl indeed stabilized the catalytically active Au<sup>3+</sup> species and inhibited the reduction of Au<sup>3+</sup> to Au<sup>0</sup>, thereby improving the activity and long-term stability of gold-based catalysts.

acetylene hydrochlorination. Among them, bimetallic supported gold catalysts showed particularly promising results.<sup>[6,8]</sup> For example, Dai et al. reported a supported gold-lanthanum catalyst on pitch-based spherical activated carbon (SAC), which was highly stable for the gas-phase hydrochlorination of acetylene, and they suggested that the addition of lanthanum to gold could weaken the occurrence of coke deposition and inhibit the valence change of gold to improve the stability of the catalyst.<sup>[6a]</sup> Wang et al. evaluated the catalytic activity and stability of Au-Cu/C and Au/C catalysts for the gas-phase catalytic hydrochlorination of acetylene, and observed greater stability of Au-Cu/C than that of Au/C.<sup>[6b]</sup> Research by Zhang et al. indicated that the additives of cobalt(III), cobalt(II), and lanthanum(III) could greatly inhibit the occurrence of coke deposition on the catalyst surface, and also inhibit catalyst sintering, thereby improving the long-term stability of goldbased/SAC catalysts.<sup>[8c]</sup> In general, gold alloyed with other metals did not significantly increase the activity. Furthermore, if the activity was increased, the catalyst deactivated much more rapidly.

Herein, a series of gold–cesium(I)/activated carbon (Au–Cs<sup>I</sup>/ AC) catalysts were carefully investigated to show the benefits of CsCl promotion of AC supporting gold catalysts for acetylene hydrochlorination. Notably, Au–Cs<sup>I</sup>/AC catalysts showed much higher catalytic activities than those of 1 Au/AC catalysts. The best catalytic performance was obtained over 1 Au–4 Cs<sup>I</sup>/ AC catalysts with an acetylene conversion of 93% and only 5% C<sub>2</sub>H<sub>2</sub> conversion loss after 50 h under the reaction conditions of temperature 180 °C and C<sub>2</sub>H<sub>2</sub> gas hourly space velocity (GHSV) of 740 h<sup>-1</sup>. The influences of CsCl doping on the redox, adsorption, and electronic properties of the Au–Cs<sup>I</sup>/AC catalysts were investigated by temperature-programmed reduction (TPR), temperature-programmed desorption (TPD) and X-ray

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photoelectron spectroscopy (XPS) techniques. Au–Cs<sup>/</sup>/AC proved to be effective catalysts for the hydrochlorination of acetylene.

### **Results and Discussion**

The time course for gas-phase hydrochlorination of acetylene over 1 Au/AC is presented in Figure 1. Similar profiles obtained



**Figure 1.** Catalytic performance of Au–Cs<sup>1</sup>/AC catalysts. Reaction conditions: T = 180 °C, C<sub>2</sub>H<sub>2</sub> GHSV = 740 h<sup>-1</sup>, feed volume ratio *V*(HCl)/*V*(C<sub>2</sub>H<sub>2</sub>) = 1.2.

over Au–Cs<sup>I</sup>/AC catalysts are also shown in Figure 1. For monometallic catalyst 1Au/AC, the maximum acetylene conversion is 84% during a reaction time of 50 h, whereas over  $1 \text{Au}-2 \text{Cs}^{1/2}$ AC catalyst the acetylene conversion is 94% during a reaction time of 5 h, which is 10% higher than that of 1 Au/AC catalysts. With a much higher cesium(I) content, the incremental extent of the acetylene conversion tends to be higher. However, if the loading amount of CsCl was more than 2 wt%, the positive effect of increasing activity was barely obtained. The turnover frequency (TOF) values of 1 Au/AC, 1 Au-0.5 Cs<sup>1</sup>/AC, 1 Au-1 Cs<sup>1</sup>/ AC, 1Au–2Cs<sup>I</sup>/AC, and 1Au–4Cs<sup>I</sup>/AC were determined to be 0.24, 0.25, 0.26, 0.27, and 0.27 s<sup>-1</sup>, respectively, and the value was slightly higher than that of the Au/C catalysts reported by Hutchings et al., though a lower amount of  $\mathsf{Au}^{3+}$  was obtained in this study than those obtained by Hutchings.<sup>[9]</sup> These results show that the coexistence of CsCl species with Au/AC is effective in increasing the activity of the catalysts.

Controlled tests for the AC support without gold showed that the activity of the  $4Cs^{I}/AC$  catalyst was identical to that of the support. The activity of AC can arise from the presence of trace amounts of K<sup>+</sup> and AI<sup>3+</sup> in the carbon matrix because these metals can display some activity in the hydrochlorination reaction of acetylene.<sup>[4b]</sup> Compared with three Au–Cs<sup>I</sup>/AC bimetallic catalysts, monometallic 1 Au/AC catalyst shows a significant rate of deactivation. The acetylene conversion of 1 Au/AC catalyst decreased from 84 to 53% after 50 h; this indicated that the 1 Au/AC catalyst had low catalyst stability under these reaction conditions. Surprisingly, the presence of CsCl species

promoted the initial catalytic activity of the 1 Au/AC catalyst and significantly enhanced the catalyst stability. In particular, the 1 Au–4 Cs<sup>1</sup>/AC catalyst displayed optimal catalytic stability for the hydrochlorination of acetylene with only 5% C<sub>2</sub>H<sub>2</sub> conversion loss after 50 h, as shown in Figure 1. These results show that an increase in the CsCl content is effective in the increase of hydrochlorination stability without significant loss of catalytic activity. It should be highlighted that, for all tests performed and reported in the current study, the selectivity to VCM was virtually 100% with only trace amounts (<0.1%) of 1,2-dichlorethane and chlorinated oligomers observed.

The long-term stability, in particular, at elevated temperatures, is crucial for the industrial application of hydrochlorination. To further demonstrate the superior performance of Au– Cs<sup>1</sup>/AC, we chose to use  $1 \text{Au}-4 \text{Cs}^{1}/\text{AC}$  to investigate the stability of the catalysts for the acetylene hydrochlorination reaction. The catalytic results are shown in Figure 2. As expected, the  $1 \text{Au}-4 \text{Cs}^{1}/\text{AC}$  catalyst showed excellent stability under the re-



**Figure 2.** Long-term stability test of  $1 \text{Au}-4 \text{Cs}^1/\text{AC}$ . Reaction conditions: T = 180 °C,  $C_2H_2$  GHSV = 50 h<sup>-1</sup>, feed volume ratio  $V(\text{HCl})/V(C_2H_2) = 1.2$ .

action conditions of 180 °C and C<sub>2</sub>H<sub>2</sub> GSHV of 50 h<sup>-1</sup>. The catalyst 1 Au–4 Cs<sup>1</sup>/AC showed more than 99.8% conversion of C<sub>2</sub>H<sub>2</sub> and more than 99.9% selectivity to VCM without any decline during a 500 h test, as demonstrated in Figure 2. The results indicated that the bimetallic 1 Au–4 Cs<sup>1</sup>/AC catalyst could give favorable activity and stability. Because reports on long-life non-mercuric catalysts are scare, the bimetallic Au–Cs<sup>1</sup> catalysts may be promising in future applications.

TPR is a useful characterization technique for the analysis of the catalysts reported herein because it is able to provide information on the quantification of the bulk  $Au^{3+}$  amount and the changes in the carbon support matrix. Figure 3 presents the H<sub>2</sub>-TPR profiles of 4Cs<sup>1</sup>/AC, 1Au/AC, and Au–Cs<sup>1</sup>/AC catalysts. For the 4Cs<sup>1</sup>/AC catalyst, a maximum hydrogen consumption peak at approximately 700 °C, which can be attributed to the reduction of the surface groups of AC, is observed. It should be noted that cesium(I) species cannot be reduced by hydrogen. The TPR profiles of fresh gold catalyst and bimetallic

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Figure 3.  $H_2\text{-}TPR$  profiles of samples a)  $4\,Cs^I/AC,$  b)  $1\,Au/AC,$  c)  $1\,Au-0.5\,Cs^I/AC,$  d)  $1\,Au-1\,Cs^I/AC,$  e)  $1\,Au-2\,Cs^I/AC,$  and f)  $1\,Au-4\,Cs^I/AC.$ 

gold-cesium(I) catalysts are different when compared with that of 4Cs<sup>1</sup>/AC, which has two hydrogen uptake bands. The band between 250 and 350 °C is the one associated with the reduction of  $Au^{3+}$ ,<sup>(10)</sup> whereas the other band between 450 and 800 °C is associated with the reduction of carbon functional groups, such as carboxyl, phenol, ether, and lactone groups.<sup>(11)</sup>

Additionally, it can be seen that the area of the Au<sup>3+</sup> band increases as the cesium(I) content increases. The area of the bands is related to the amount of Au<sup>3+</sup> present in the samples. By comparing the thermal conductivity detector (TCD) signals with that of a standard, the fractions of Au<sup>3+</sup> species in these fresh catalysts can be estimated. It is worth mentioning that the relative amount of Au<sup>3+</sup> in Au–Cs<sup>I</sup>/AC catalysts increases as the Cs<sup>I</sup> content increases (Figure 4). By analyzing the amount of Au<sup>3+</sup> for the fresh 1 Au/AC catalyst and the Au–Cs<sup>I</sup>/ AC catalyst, the Au<sup>3+</sup> content increased from approximately 16.2% to 21.1, 26.8, 35.9, and 46.8%, respectively, for Cs<sup>I</sup> contents from 0, 0.5, 1, 2, to 4. Owing to the catalyst preparation procedure, which, after impregnation with the same gold loading, no filtering of the carbon or catalyst washing was per-



**Figure 4.** The proportional content of  $Au^{3+}$  species for 1 Au/AC and Au–Cs<sup>1</sup>/AC catalysts prepared with different Cs<sup>1</sup> content.

formed, the gold metal loading should be considered as equal to the nominal amount of metal impregnated onto the support. Thus, the increase in Au<sup>3+</sup> could be explained by the increasing Cs<sup>1</sup> content in the samples; Au particles preferentially exist in the Au<sup>3+</sup> state. This also shows that, if the amount of  $Au^{3+}$  increases (in the range of 16.2 to 26.8), the activity also increases. It is worth noting that, in a previous study,<sup>[12]</sup> material prepared at 110°C in the presence of aqua regia presented higher amounts of Au<sup>3+</sup> than those in the present study; this could be attributed to the drying process employed, which was under vacuum, rather than air drying used in this study. However, if the amount of Au<sup>3+</sup> increases further, no actual gain in activity is obtained. According to Hutchings et al., increasing amounts of Au<sup>3+</sup>, which are clearly needed for the reaction, will not further increase the activity after exceeding a given threshold.<sup>[9]</sup> By using TPR determinations, the optimal Au<sup>3+</sup> amount would be approximately 30%, and excess amounts would not affect the reactivity of the catalyst.<sup>[13]</sup> This was explained by the existence of active sites at the Au/C interface, and not just by the presence of Au<sup>3+</sup> species on top of the Au nanoparticles.<sup>[9,12]</sup> It also can be seen that, as the additive amount of Cs<sup>1</sup> increases, a positive shift of the reduction band of Au<sup>3+</sup> occurs. This shows the existence of interactions between the gold and cesium(I) species. The reduction behavior of Au<sup>3+</sup> is affected by Au-Cs<sup>1</sup> interactions. The presence of CsCl makes it difficult to reduce Au<sup>3+</sup> species. Therefore, these results indicate that a synergistic effect between Au and Cs exists in Au-Cs<sup>I</sup>/AC catalysts. It is reasonable to conclude that the addition of CsCl can stabilize the catalytic active Au<sup>3+</sup> species and inhibit the reduction of Au<sup>3+</sup> into Au<sup>0</sup> during the preparation process.

TPD is an effective technique that provides a direct comparison of the adsorption and activation of reactants on different catalysts. Specifically, the desorption temperature in the TPD profiles reflects the binding strength of the adsorbed species; the catalyst surface and peak area correlate with the amount of active species. Figure 5 presents the  $C_2H_2$ -TPD profiles for AC, 1 Au/AC, and bimetallic Au–Cs<sup>1</sup>/AC catalysts with various



Figure 5. TPD profiles of acetylene on different samples: a) AC (support), b) 1 Au/AC, c) 1 Au-0.5 Cs<sup>1</sup>/AC, d) 1 Au-1 Cs<sup>1</sup>/AC, e) 1 Au-2 Cs<sup>1</sup>/AC, and f) 1 Au-4 Cs<sup>1</sup>/AC.



Cs<sup>1</sup> contents. AC shows a weak desorption peak at approximately 115 °C, which is related to acetylene desorption from the support. After the deposition of 1 wt% gold onto the AC support, a new C<sub>2</sub>H<sub>2</sub> desorption peak appears at 252°C. Because there is no desorption peak below 180 °C, only C<sub>2</sub>H<sub>2</sub> desorption at a higher temperature is considered. Interestingly, the relative content of C<sub>2</sub>H<sub>2</sub> desorption in the Au-Cs<sup>1</sup>/AC bimetallic catalysts increases monotonically with Cs<sup>1</sup> content (Figure 5), which indicates that the quantity of active  $Au^{3+}$  species increases with Cs<sup>1</sup> content. Because the areas of C<sub>2</sub>H<sub>2</sub>-TPD peaks can be correlated with the amounts of active species, an increase in the amount of active sites is evidenced by the increase in  $C_2H_2$  desorption. Taking both  $C_2H_2$ -TPD and  $H_2$ -TPR measurements into account, we can confirm that not only the amounts of Au<sup>3+</sup> active species increase as the Cs<sup>1</sup> content increases, but they can also be accessible for acetylene adsorption. In addition, it is known that weakly bound species have a lower activation energy for desorption and will therefore undergo desorption at a lower temperature. Thus, the shift in the higher C<sub>2</sub>H<sub>2</sub> desorption temperature to lower temperature may be attributed to the interaction between Au and Cs<sup>+</sup> in bimetallic catalysts, resulting in different C2H2 chemisorption strengths and further catalytic properties than those of monometallic  $1\,\mathrm{Au}/\mathrm{AC}$ 

Because previous literature studies ascribed the activity of the catalyst to the presence of Au<sup>3+</sup> species and postulated that they were the active sites,<sup>[2,4a,5a,b,13]</sup> XPS was used to investigate the valence-state changes of the surface of the Au nanoparticles and the relative amount of active Au<sup>3+</sup> in 1Au/AC and bimetallic 1Au–4Cs<sup>1</sup>/AC catalysts before and after the reaction. More than one gold species was evident, and thus, curve fitting was employed to determine the ratio of each species (Figure 6). Owing to the reduction property of carbon towards Au<sup>3+</sup>, there is a large amount of Au<sup>0</sup> in both fresh 1Au/AC and 1Au–4Cs<sup>1</sup>/AC catalysts. In fresh 1Au/AC and 1Au–4Cs<sup>1</sup>/AC catalysts, the relative content of Au<sup>3+</sup> is 11.0 and 35.8%, respectively, which is slightly lower than the H<sub>2</sub>-TPR results.

For one reason, the  $Au^{3+}$  amounts obtained by XPS are lower than those obtained by H<sub>2</sub>-TPR can be ascribed to the former being a surface method, whereas the latter is a bulk technique. For another reason, XPS is known to cause chemical and structural changes within several investigated molecules.<sup>[14]</sup> The technique has been reported to result in the reduction of metal ions by ion, electron, and photon bombard-



Figure 6. XPS spectrum and simulation for the samples a) fresh 1Au/AC catalyst, b) used 1Au/AC catalyst, c) fresh 1Au–4Cs<sup>1</sup>/AC catalyst, and d) used 1Au–4Cs<sup>1</sup>/AC catalyst.

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ment, referred to as "radiation-induced damage" during analysis. For example, Karadas et al. published an overview of the  $HAuCl_4$  photoreduction process from  $Au^{3+}$  to  $Au^0$  when exposed to 1253.6 eV Mg<sub>Ka</sub> (non-monochromatized) radiation.<sup>[15]</sup> Together with further contributions from Ozkaraoglu et al.,<sup>[16]</sup> Karadas and co-workers showed that the disappearance of Au<sup>3+</sup> peaks in the XPS spectra occurred through first-order kinetics, but at differing rates. In view of this, it is reasonable that the Au<sup>3+</sup> content obtained by XPS is always lower than those obtained by TPR. It should also be stressed that some small metallic gold clusters (Au<sup>0</sup>) are also formed in the fresh gold-base catalyst (Figure 6). However, the Au<sup>0</sup> species are inactive and are not involved in the reaction.<sup>[9]</sup> In addition, the higher content of Au<sup>3+</sup> in 1Au-4Cs<sup>I</sup>/AC also illustrated that the existence of CsCl inhibited the reduction of Au<sup>3+</sup> into Au<sup>0</sup> in the preparation process. Under the reaction conditions,  $Au^{3+}$  is reduced into  $Au^{0}$ , which contributes to the deactivation of the gold catalyst. In the case of the 1Au/AC catalyst after the reaction, only 6.3% of Au<sup>3+</sup> species are present, which demonstrates that a reduction and/or agglomeration of Au<sup>3+</sup> species occurs in the reaction process. On the contrary, there is a considerable amount of  $Au^{3+}$  (26.3%) in the used 1Au-4Cs<sup>I</sup>/AC catalyst, which indicates that the addition of CsCl indeed inhibits the reduction of Au<sup>3+</sup> to Au<sup>0</sup>.

The  $Au^{3+}$  content after the reaction was also determined for 1 Au/AC and 1 Au–4 Cs<sup>I</sup>/AC catalysts by means of TPR. Figure 7



Figure 7. TPR intensities for the reduction of  $Au^{3+}$  species for used 1Au/AC (a) and  $1Au-4Cs^{1}/AC$  (b) catalysts.

shows the TPR profiles for the 1Au/AC and 1Au–4Cs<sup>1</sup>/AC catalysts after the reaction. It is clear from TPR analysis of the 1Au–4Cs<sup>1</sup>/AC catalyst that the low-temperature reduction peak, which is characteristic of Au<sup>3+</sup>, can be clearly observed; this indicates that Cs<sup>1</sup> exerts a negative influence on the ease of Au<sup>3+</sup> reduction, which occurs during the reaction process. As in the case of 1Au/AC, the reduction peak of Au<sup>3+</sup> to Au<sup>0</sup> is evidently decreased compared with that of the fresh one, which shows a higher degree of Au<sup>3+</sup> reduction to Au<sup>0</sup> during acetylene hydrochlorination. Also, by comparing the TCD signals with a standard, the fractions of Au<sup>3+</sup> species in these

used catalysts can be estimated. After the reaction, the Au<sup>3+</sup> content of the 1Au/AC catalyst reduces to about 7.6%. On the contrary, after the addition of Cs<sup>1</sup> to the Au catalyst, the Au<sup>3+</sup> content of the 1Au–4Cs<sup>1</sup>/AC catalyst only reduces to about 32.1%, which further confirms that the addition of CsCl is preferential to stabilize catalytic active Au<sup>3+</sup> species and inhibit the reduction of Au<sup>3+</sup> to Au<sup>0</sup> in gold–base/AC catalysts during the reaction process.

## Conclusion

Bimetallic Au-Cs<sup>I</sup>/AC catalysts with varying weight ratios of Cs<sup>1</sup>/Au from 0.5 to 4 exhibited remarkably higher catalytic activity and stability than that of a monometallic 1 Au/AC catalyst in the hydrochlorination of acetylene. The addition of the second metal component allowed catalysts to be prepared with Au<sup>3+</sup> abundance on the catalyst surface. Catalytic tests of acetylene hydrochlorination showed a dramatic increase in the activity to vinyl chloride when the Cs<sup>1</sup>/Au weight ratio increased from zero to two, with no further improvement in activity. The catalytic stability could be further enhanced upon increasing the weight ratio from two to four. It was indicated that the addition of CsCl was preferential to stabilize the catalytically active Au<sup>3+</sup> species and inhibit the reduction of Au<sup>3+</sup> to Au<sup>0</sup> in both the preparation and reaction process for goldbased/AC catalysts, thereby improving the activity and longterm stability of the gold-based catalysts. Clarification of the influence of the addition of CsCl on stabilizing the catalytically active Au<sup>3+</sup> species requires a further detailed investigation, which is currently underway in our laboratory.

## **Experimental Section**

#### **Catalyst preparation**

A commercially available AC, NORIT ROX 0.8 (pellets of 0.8 mm in diameter and 5 mm long), was selected for the preparation of the support. The AC was first pretreated with HNO<sub>3</sub> (65 wt %) at room temperature for 1 h to remove Na, Fe, and Al contaminants. The pretreated AC was filtered, washed with deionized water until pH 7, and then dried at 110 °C for 12 h.

Bimetallic Au-Cs<sup>I</sup>/AC catalysts were prepared by using an incipient wetness impregnation technique. The Au and Cs<sup>1</sup> precursors, HAuCl<sub>4</sub>·4H<sub>2</sub>O (assay: 48%) and CsCl (99.9 wt%) powder, were first dissolved in aqua regia and the solution was added dropwise to the pretreated AC support with agitated stirring (dropwise addition of the solution to the support with stirring and then the addition of a second drop of solution after the first liquid was completely dispersed into the support). After the solution was homogeneously mixed with the support, the system was aged at 40 °C for 4 h, followed by drying at 110 °C in air for 12 h before use. Au loading in all catalysts was fixed at 1.0 wt% at various Au/Cs<sup>1</sup> ratios (wt/wt), namely, 1:0.5, 1:1, 1:2, and 1:4, and were denoted as 1 Au-0.5 Cs<sup>1</sup>/ AC, 1Au–1Cs<sup>1</sup>/AC, 1Au–2Cs<sup>1</sup>/AC, and 1Au–4Cs<sup>1</sup>/AC, respectively. The same procedure was also followed to prepare the corresponding 1Au/AC (1.0 wt% Au loading) and 4Cs<sup>I</sup>/AC (4.0 wt% Cs<sup>I</sup> loading) catalysts for comparison.

#### **Catalyst characterization**

XPS analysis was performed by using a Kratos AXIS Ultra DLD spectrometer with a monochromatized aluminum X-ray source (1486.6 eV) and a pass energy of 40 eV. The pressure in the sample analysis chamber was lower than  $6 \times 10^{-9}$  torr during data acquisition. The C 1s peak at 284.8 eV, which arose from adventitious carbon, was taken as a reference to correct surface-charging effects. This reference gave binding energy values with a precision of  $\pm$  0.02 eV.

TPD experiments were performed in a tubular quartz reactor. The samples (75 mg) were first treated in situ at 180 °C for 0.5 h by using pure  $C_2H_2$  and then the sample was swept with pure Ar at a flow rate of 30 mL min<sup>-1</sup> for 1 h to remove physisorbed and/or weakly bound species. TPD was performed by heating the sample from room temperature to 550 °C at a ramp rate of 10 °C min<sup>-1</sup> in pure Ar, and the TPD spectra were recorded by using a quadrupole mass spectrometer (QMS 200 Omnistar).

TPR experiments were performed in the same apparatus as that used for the TPD experiments. The weight of the tested samples was 75 mg. The temperature was linearly increased from 30 to 850 °C at a rate of 10 °C min<sup>-1</sup>, under a flow of hydrogen (5% in Ar, 40 cm<sup>3</sup> min<sup>-1</sup>). The hydrogen consumption was measured by using a TCD.

#### **Catalyst tests**

Catalysts were tested for acetylene hydrochlorination in a fixedbed glass microreactor (i.d. 10 mm). Acetylene (5 mLmin<sup>-1</sup>, 1 bar) and hydrogen chloride (6 mLmin<sup>-1</sup>, 1 bar) were fed by means of a mixing vessel through calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), with a total  $C_2 H_2\,$  GHSV of 740  $h^{-1}.$  A reaction temperature of 180  $^\circ C\,$  was chosen; blank tests with 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 first passed through an absorption bottle containing a solution of NaOH and then analyzed online by means of a GC equipped with a flame ionization detector (FID). Chromatographic separation and identification of the products was performed by using a Porapak N packed column (6 ft×1/800 stainless steel). The long-term stability experiments were performed in the same apparatus under reaction conditions of 180 °C and  $C_2H_2$  GSHV of 50 h<sup>-1</sup>.

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