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Nitrogen-modified activated carbon supported bimetallic Gold-Cesium(I) as highly active and stable catalyst in the hydrochlorination of acetylene

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Abstract: In the challenging acetylene hydrochlorination to vinyl chloride over Au-base catalysts, Au-Cs\textsuperscript{3+} catalysts are substantially more active and stable than their monometallic counterparts. Here we describe a novel nitrogen-modified activated carbon supported Au-Cs\textsuperscript{3+} catalyst (1Au4Cs\textsuperscript{3+}/NAC) delivers stable performance with acetylene conversion reaching 90.1% and there was only 1.5% C\textsubscript{2}H\textsubscript{2} conversion loss after 50 h under the reaction conditions of C\textsubscript{2}H\textsubscript{2} hourly space velocity 1480 h\textsuperscript{-1}. After a careful characterization of all the catalysts, we concluded that the nitrogen atoms influence the stability of the Au-Cs\textsuperscript{3+} catalysts correlate with the strengthening the adsorption of hydrogen chloride to the catalyst and consequently inhibiting Au\textsuperscript{3+} reduction under reaction conditions.

Introduction

Acetylene hydrochlorination is an important coal-based technology for the industrial production of vinyl chloride.\textsuperscript{1} Supported mercury chloride (HgCl\textsubscript{2}) catalysts are currently the most convenient and the most practical catalysts for hydrochlorination of acetylene, but HgCl\textsubscript{2} is susceptible to reduction by acetylene and sublimation, which severely limits the production capacity and causes severe environmental problems.\textsuperscript{2} The catalysts free from toxic mercury are thus desired.

Since Hutchings et al. carried out pioneering work to investigate the use of non-mercury catalysts for acetylene hydrochlorination,\textsuperscript{3-5} a significant number of supported-metal chlorides catalysts, including Bi\textsuperscript{3+},\textsuperscript{6} Cu\textsuperscript{2+},\textsuperscript{7} Pt\textsuperscript{2+},\textsuperscript{8} and Pd\textsuperscript{2+} chlorides,\textsuperscript{9} displaying considerable activity toward catalyzing the acetylene hydrochlorination, and the most widely used are based on supported AuCl\textsubscript{3} often in combination with other metal chlorides owing to its high intrinsic activity toward the formation of the desired vinyl chloride.\textsuperscript{10-12} However, the deactivation rate of the AuCl\textsubscript{3} catalyst is still very high when the reaction used is a real commercial condition with lifetimes in the range of few hours.\textsuperscript{5} The practical application of Au catalysts for hydrochlorination reaction is attractive but, at present, it is still desired that the stability should be improved.

Recently, Nitrogen-doped carbon materials have attracted considerable attention as new promising materials.\textsuperscript{13} The presence of nitrogen atoms in the carbonaceous material tailors their surface properties accordingly, supporting a new idea to employ it as one active catalyst for mercury-free hydrochlorination.\textsuperscript{14,15} In addition, recently Dai et al. reported that AuCl\textsubscript{3}/PPy-MWCNTs catalyst showed the benefits of the nitrogen promotion of Au\textsuperscript{3+} catalysts.\textsuperscript{16} The enhanced catalytic performance was attributed to electron transfer from PPy to the Au\textsuperscript{3+} center, which increased the adsorption of hydrogen chloride. We have recently contributed to the field of Au-catalyzed acetylene hydrochlorination by discovering that the use of Cs\textsuperscript{3+} as a promoter can facilitate more efficient Au\textsuperscript{3+} active species stabilization under much harsher conditions.\textsuperscript{17} These findings are useful for the design of highly active and stable acetylene hydrochlorination catalysts and have prompted us to consider whether the nitrogen-promoting effect can be applied to bimetallic catalysts, to give further improved performance in the acetylene hydrochlorination reaction. In this work the effect of modification of nitrogen to activated carbon supported Au-Cs\textsuperscript{3+} catalysts has been investigated by synthesizing a 1Au4Cs\textsuperscript{3+}/NAC catalyst and evaluating the material properties by several characterization techniques (XPS, STEM, TPD, TPR) comparing it to 1Au4Cs\textsuperscript{3+}/AC catalysts as reference.

Experimental

Materials

Activated carbon (marked as AC, NORIT ROX 0.8, pellets of 0.8 mm diameter and 5 mm length); HAuCl\textsubscript{4} • 4H\textsubscript{2}O (the content of Au assay 49.7%); urea (99 wt.%); CsCl (99.9 wt.%); H\textsubscript{2}O\textsubscript{2} (10 wt.%); glacial acetic acid (10 wt.%); C\textsubscript{2}H\textsubscript{2} (gas, 98%); HCl (gas, 99.999%).

Catalyst preparation

A commercially activated carbon NORIT ROX 0.8 was selected for the preparation of support. The activated carbon was first pretreated with HNO\textsubscript{3} (65 wt.%) at room temperature for 1 h. Subsequently, it was filtered, washed and then dried at 110 °C for 12 h (sample AC).

N-doped AC was prepared based on the process described...
A mixture of AC (5 g), glacial acetic acid (3 mL) and distilled water (50 mL) was stirred for 30 min to obtain carbon slurry. Urea (3 g), H$_2$O$_2$ (10 mL) and deionized water (30 mL) were added, and the solution was stirred for 24 h at room temperature in the dark. Finally, the solution was filtered and calcined at 500 °C under a nitrogen atmosphere for 1 h. The obtained sample was labeled as NAC.

Supported bimetallic Au-Cs catalysts were prepared using an incipient wetness impregnation technique. A HAuCl$_4$·4H$_2$O and CsCl solution in aqua regia was added dropwise to the NAC or AC 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 drying at 110 °C for 12 h for use. The obtained catalysts were labeled as 1Au4Cs$^\text{I}$/NAC and 1Au4Cs$^\text{I}$/AC, respectively. Au loading in all the catalysts was fixed at 1.0 wt.%.

**Catalyst characterization**

The sizes of particles on samples were also observed by a transmission electron microscope (TEM, Tecnai G2 F30 S-Twin, 300 kV). The solid samples were finely ground. The resultant fine powders were dispersed ultrasonically in the ethanol and then loaded on a copper grid (Beijing Zhongjingkeyi Technology Co., Ltd.).

The elemental surface composition of the catalysts was controlled by XPS acquired with a Kratos AXIS Ultra DLD spectrometer. XPS analysis was performed with the monochromatized aluminum X-ray source and pass energy of the 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.

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 HCl and then cooled to room temperature in the same atmosphere. The sample was swept with pure Ar at a flow rate of 30 ml/min 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 were recorded by a quadrupole mass spectrometer (QMS 200 Omnistar).

Temperature-programmed reduction (TPR) experiments were carried out on a micro-flow reactor fed with a flow of hydrogen (5% in Ar) at a rate of 40 ml min$^{-1}$. The weight of the tested samples was (about) 75 mg. 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).

**Catalytic test**

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass microreactor (i.d. 10 mm). Acetylene (10 mL min$^{-1}$, 1 bar) and hydrogen chloride (12 mL min$^{-1}$, 1 bar) were fed through a mixing vessel via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), with a total GHSV (C$_2$H$_2$) of 1480 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 NaOH solution to remove excess HCl first and then analysed on-line by GC equipped with a flame ionisation detector (FID). Chromatographic separation and identification of the products was carried out using a Porapak N packed column.

**Results and discussion**

Fig.1 XPS spectra of (a) fresh 1Au4Cs$^\text{I}$/AC and 1Au4Cs$^\text{I}$/NAC samples normalized at 284.8 eV of C1s, (b) N1s spectrum for the fresh 1Au4Cs$^\text{I}$/NAC catalyst.

The XPS results shown in Fig. 1a confirm the elemental compositions of 1Au4Cs$^\text{I}$/AC and 1Au4Cs$^\text{I}$/NAC samples. The peaks at about 86.1, 200.6, 284.8, 399.5, and 725.6 eV can be assigned to the binding energy of Au4f, Cl2p, C1s, N1s, O1s and Cs3d, respectively. The XPS spectrum of AC indicates that as the annealing temperature increases to 500 °C with doping carbon with nitrogen atoms, the nitrogen signal can be clearly detected. Fig. 1b demonstrates the high-resolution XPS spectra based on the deconvoluted N1s spectra. The peak at 398.6, 400.4, 402.7 eV corresponds to pyridinic N, pyrrolic N and quaternary N, respectively. XPS analysis (Fig. 1b) reveals that three types of nitrogen species coexist in the 1Au4Cs$^\text{I}$/NAC catalyst. Recent observations suggest that carbon-based catalyst support materials can be systematically doped with nitrogen to create strong, beneficial catalyst-support interactions by increased support/catalyst chemical binding (or anchoring) which substantially enhances catalyst activity and stability.

The gold content by mass of the catalysts as determined by ICP-MS was 0.94 +/- 0.07 wt% for 1Au4Cs$^\text{I}$/AC and 0.95 +/-
0.05 wt% for 1Au4Cs/\text{NAC}. Fig. 1 shows two typical TEM micrographs. The small bright dots represent the metal particles; particles below 5 nm are dominant in 1Au4Cs/\text{AC}, though some are found up to 6 nm in diameter (Fig. 2a). In contrast, particles below 3 nm are dominant in 1Au4Cs/\text{NAC} (Fig. 2b). Especially 1Au4Cs/\text{AC} showed a large particle size distribution. Most of the particles in 1Au4Cs/\text{AC} had particle sizes below 4 nm, with a small fraction between 4 and 6 nm. For 1Au4Cs/\text{NAC}, hardly any particles larger than 4 nm were observed. The average particle size for 1Au4Cs/\text{AC} was 3.7 nm and for 1Au4Cs/\text{NAC} 2.3 nm. This indicates that adding nitrogen atoms had caused a decrease in Au NPs particle size.

The catalytic performance of Au-base catalysts for acetylene hydrochlorination is shown in Fig. 3. To accelerate the deactivate process of Au-based catalysts, higher GHSV (1480 h\(^{-1}\)) was carried out than that reported in the literature. NAC catalysts display very poor catalytic activity (5% conversion) for acetylene hydrochlorination reaction (not shown), while no conversion was detected in AC. In fact, experimental studies and theoretical simulations revealed that the carbon atoms bonded with pyrrolic nitrogen atoms as active sites can deliver limited activity have been reported by Bao’s group before.\(^{15}\)

The catalyst evaluation data in Fig. 3b shows that 1Au4Cs/\text{AC} had good performance with the acetylene conversion of 1Au4Cs/\text{AC} catalyst decreases from 89.2% down to 80.1% after running for 50 h, indicating that 1Au4Cs/\text{AC} is slightly deactivated under this reaction conditions. As a comparison, the 1Au4Cs/\text{NAC} catalyst exhibits a similar initial performance with 1Au4Cs/\text{AC}, and its C\(_2\)H\(_2\) conversion reaches 90.1% at 4 h (Fig. 3a). At the same time, 1Au4Cs/\text{NAC} had stable conversion without significant decline in activity is observed in the reaction time (89.6% at 50 h). Thus, the results suggest that the nitrogen-doped catalysts (1Au4Cs/\text{NAC}) exhibited improved catalytic stability as well as a slightly increased catalytic activity. This indicates the effectiveness of nitrogen doping in tuning the reactivity. Dai and coworkers\(^{18}\) have indicated an improved activity and stability upon the addition of nitrogen atoms to Au-based acetylene hydrochlorination catalysts (AuCl\(_3\)/PPy-MWCNT). On the one hand, it has been reported that the incorporation of nitrogen atoms increased the electron density of the Au\(^{3+}\) center via the transfer of lone pair electrons on the nitrogen atom to the Au\(^{3+}\) center. On the other hand, Au\(^{3+}\) species is the electron donor in the adsorption process of hydrogen chloride. Thus, it is most likely that this promoting effect of 1Au4Cs/\text{NAC} bimetallic catalysts during acetylene hydrochlorination is related to the increased electron-donating capability of Au\(^{3+}\) for hydrogen chloride adsorption, which is due to the increased electron density of Au\(^{3+}\) as a result of electron transfer from nitrogen atom. This will be discussed in the HCl-TPD analysis. It should be highlighted that for all the tests carried out and reported in the current study, the selectivity to vinyl chloride was virtually 100% with trace amounts (< 0.1%) of 1,2-dichloroethane and chlorinated oligomers only throughout the entire run period according to the spectrum of TCD.

Fig. 4 shows the TPR profiles for the fresh and used Au-base catalysts. For all the catalysts, a distinguishable hydrogen
consumption peak in the range of 400-800 °C can be observed, which can be attributed to the reduction of the surface groups of activated carbon at the carbon surface, which releases CO and CO₂ with concomitant reduction of oxygenated groups by H₂ in the TPR stream. More specifically, the profile can be fitted with two contributions. The reduction bands in the range of 400-650 °C can be assigned to the decarboxylation reactions of carboxylic acids and carboxylic anhydrides groups, while above 650 °C, these are likely due to the reduction of lactones and phenols. As mentioned before, this phenomenon on the carbon matrix should be considered a consequence of using HNO₃ in the washing step, which induced modifications on the carbon surface inducing oxygenated functional groups, as well as changes in the textural properties of the carbon support. In addition, the analysis of 1Au4Cs/AC sample led to assign the reduction band around 322 °C to Au³⁻ to Au⁰ (Fig. 4a). Besides, a straightforward decrease of temperature in the reduction band of Au³⁻ to 309 °C was observed (Fig. 4b) for 1Au4Cs/NAC, this shifts indicate strong interactions between Au species and nitrogen atoms exists in 1Au4Cs/NAC catalysts. Through comparing the TCD signals with a standard, the fractions of different Au species in these fresh catalysts can be estimated. This allows an estimation of ca.46.8, and 38.8% for the 1Au4Cs/AC and 1Au4Cs/NAC catalysts, respectively. As in the case of used 1Au4Cs/AC, the reduction peak of Au³⁻ to Au⁰ is evidently decreased comparing with the fresh one, which shows a degree of Au³⁻ reduction to Au⁰ during acetylene hydrochlorination. In contrast, the reduction peak of Au³⁻ to Au⁰ is negatively observed for 1Au4Cs/NAC comparing with the fresh one. Also through comparing the TCD signals with a standard, this allows an estimation of ca. 27.8 and 36.2% for the used 1Au4Cs/AC and 1Au4Cs/NAC catalysts, respectively. This result showed that the presence of nitrogen atoms in the 1Au4Cs/NAC catalyst partly inhibited the reduction of Au³⁻, which can further stabilize the catalytic active Au³⁺ species in the reaction process of AuCl₃ catalysts. This result is consistent with the excellent catalytic activity and stability of the 1Au4Cs/NAC catalyst. It is worth noting that the result revealed in this study, i.e., that the 1Au4Cs/AC presents higher amount of Au³⁺ compared with the 1Au4Cs/NAC, however, the activity of 1Au4Cs/AC is no more than 1Au4Cs/NAC. In fact, according to Hutchings et al., the increasing amount of Au³⁺, being clearly needed for the reaction, exceeding a given threshold will not further increase the activity. By using TPR determinations, the optimal Au³⁺ amount would be about ca. 30 %, with excess amounts not affecting the reactivity of the catalyst, which is consistent with the catalytic performance of 1Au4Cs/AC and 1Au4Cs/NAC catalysts (see Fig. 3).

Since previous literature studies ascribed the activity of the Au-base catalyst to the presence of Au³⁺ species postulating them as active sites. In order to obtain a correlation on the activity of VCM production with the amount of Au³⁺ species clusters made on the catalyst surface and the valence state changes of the catalyst structure before and after the reaction, samples tested for the acetylene hydrochlorination at different composition were then carefully analysed by XPS. It should be noted that where more than one Au species was evident, curve fitting was employed to determine the ratio of each species (Fig. 5). The XPS spectra of Au 4f level for all samples were deconvoluted into three pairs of peaks for Au³⁺, Au⁰ and Au²⁻ species, respectively. Table 1 lists the binding energy and the relative content of each Au species in the fresh and used catalysts. The full-width-half-maximum (FWHM) values of Au peaks were also

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Fig.5 XPS spectrum and simulation for the samples: (a) fresh 1Au4Cs/AC catalyst, (b) used 1Au4Cs/AC catalyst, (c) fresh 1Au4Cs/NAC catalyst, (d) used 1Au4Cs/NAC catalyst.
summarized in Table 1. It is worth mentioning that the FWHM of Au\(^{3+}\) peaks obtained for both fresh and used bimetallic catalysts are very close. Due to the reduction property of carbon towards Au\(^{3+}\), there is a large number of Au\(^{0}\) in fresh Au-base catalysts (Table 1). It should also be stressed that some small metallic gold clusters (Au\(^{0}\)-s) are also formed in the fresh 1Au4Cs/AC and 1Au4Cs/NAC catalyst, which coincided well with the previous publications. However, the Au\(^{0}\)-s species are inactive and not involving in the reaction, since the reduced catalysts also contain these Au\(^{0}\)-s clusters and they displayed negligible catalytic activity (< 5% conversion) for acetylene hydrochlorination under the same conditions (not shown), illustrating that the presence of Au\(^{3+}\) was indispensable for high catalytic activity and the Au\(^{0}\)-s species are inactive and not involving in the reaction. It has also been confirmed by other researchers that reduced Au-base catalysts containing only Au\(^{0}\)-s and Au\(^{0}\) clusters can not activate acetylene directly. In fresh 1Au4Cs/AC and 1Au4Cs/NAC samples, the relative content of Au\(^{3+}\) is 32.6% and 31.4%, respectively (Table 1). The higher content of Au\(^{3+}\) in 1Au4Cs/AC can be observed. Under the reaction conditions, Au\(^{3+}\) is reduced into Au\(^{0}\), contributing to the deactivation of the Au catalyst. In the case of 1Au4Cs/AC catalysts after reaction, only 20.5% Au\(^{3+}\) species presents (Table 1), demonstrating that a reduction and/or agglomeration of Au\(^{3+}\) species occurs in the reaction process. In contrary, in the used 1Au4Cs/NAC catalyst, there are still large amounts of Au\(^{3+}\) (30.6%), indicating that the incorporation of the nitrogen atoms helps to keep the active Au\(^{3+}\) species stable at high temperature under reducing atmosphere. The Au\(^{3+}\) amount obtained by XPS are lower than those obtained by H\(_2\)-TPR can be ascribed to that XPS is known to cause chemical and structural changes within several investigated molecules. For example, Karadas published an overview of the HAuCl\(_4\) photoreduction process from Au\(^{3+}\) to Au\(^{0}\) when exposed to 1253.6 eV Mg K\(_\alpha\) (nonmonochromatized) radiation. Together with further contributions from Ozkaraouglu et al., Karadas and co-workers showed that the disappearance of Au\(^{3+}\) peaks in the XPS spectra occur via first-order kinetics but at differing rates. In view of this, the content of Au\(^{3+}\) obtained by XPS always lower than those obtained by TPR is reasonable.

In combination with the catalytic performances of these catalysts (Fig. 3), it is reasonable to conclude that a high content of Au\(^{3+}\) leads to the best catalytic performance, as displayed by the 1Au4Cs/NAC.

### Table 1: Quantification and identification from XPS of Au species over Au-base catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Au species (%)</th>
<th>(Binding energy) (\pm) (FWHM) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Au^{3+})</td>
<td>(Au^{0})</td>
</tr>
<tr>
<td>1Au4Cs/AC fresh</td>
<td>32.6</td>
<td>59.2</td>
</tr>
<tr>
<td></td>
<td>(86.7) (\pm) (1.4)</td>
<td>(84.3) (\pm) (1.3)</td>
</tr>
<tr>
<td>1Au4Cs/AC used</td>
<td>20.5</td>
<td>66.5</td>
</tr>
<tr>
<td></td>
<td>(86.7) (\pm) (1.5)</td>
<td>(84.3) (\pm) (1.4)</td>
</tr>
<tr>
<td>1Au4Cs/NAC fresh</td>
<td>31.4</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>(87.0) (\pm) (1.4)</td>
<td>(84.3) (\pm) (1.2)</td>
</tr>
<tr>
<td>1Au4Cs/NAC used</td>
<td>30.6</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>(87.3) (\pm) (1.5)</td>
<td>(84.8) (\pm) (1.1)</td>
</tr>
</tbody>
</table>

Fig. 6 TPD profiles of hydrogen chloride on different samples: (a) 1Au4Cs/AC and (b) 1Au4Cs/NAC.

HCl-TPD is also used to characterize the active sites for the hydrogen chloride adsorption. As shown in Fig. 6, the 1Au4Cs/AC and 1Au4Cs/NAC catalysts presented a band between 50 and 400 °C, which was characteristic of hydrogen chloride desorption. However, the areas of the HCl-TPD peaks for the 1Au4Cs/NAC catalyst were much larger than for 1Au4Cs/AC catalyst. This suggested that the increase in chemisorbed hydrogen chloride on 1Au4Cs/NAC compared with 1Au4Cs/AC. The observed adsorption was caused by the interaction between nitrogen and Au\(^{3+}\), which changed the nature of the catalyst itself. The favorable adsorption of hydrogen chloride on 1Au4Cs/NAC can be explained by the transfer of nitrogen \(\pi\) electrons to the empty orbital of gold, which enhanced the electron-donating ability of gold and allowed the catalyst to combine with more hydrogen chloride.

It is reported in the literature that when hydrogen chloride and acetylene coadsorbed on the AuCl, the acetylene was co-catalyzed by hydrogen chloride and the AuCl to produce vinyl chloride. In contrast, if the hydrogen chloride in the gas phase could not adsorb on the Au sites, the intermediate chlorovinyl was difficult to desorb from the AuCl catalyst that resulted in the side reaction and the rapid deactivation of the AuCl due to the loss of Cl atoms and consequently loses its activity. Based on the above understanding, the adsorption of hydrogen chloride is very important for the stability of AuCl catalyst, for one thing, is beneficial for improving the catalytic activity, for another, hydrogen chloride can remain Au in its oxidative state and inhibit the active Au\(^{3+}\) species reduced by C\(_2\)H\(_2\). Thus, it is clearly that doping of carbon materials with nitrogen atoms can enhance the adsorption of hydrogen chloride and activate acetylene, and hence the hydrochlorinination of acetylene.

### Conclusions

In summary, we have successfully demonstrated that the doping of nitrogen can efficiently further enhance the catalytic...
performance of Au-Cs\textsuperscript{1} bimetallic catalysts. The doped 1\textsuperscript{Au4Cs}/NAC catalysts with a total nitrogen content of 2.9 wt.\% are quite stable and more active for the hydrochlorination of acetylene. The enhanced catalytic performance may due to that nitrogen atoms strongly interacted with Au species and strengthened the ability of the resultant catalysts to adsorb hydrogen chloride and inhibit the reduction of Au\textsuperscript{0} to Au\textsuperscript{3+} during acetylene hydrochlorination and hence improve the catalytic stability. The excellent catalytic performance of the 1\textsuperscript{Au4Cs}/NAC catalyst demonstrated its potential as an alternative to mercury chloride catalysts for acetylene hydrochlorination.

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Notes and references

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15. X. Li, X. Pan, L. Yu, P. Ren, X. Wu, L. Sun, F. Jiao, X. Bao, Silicon carbide-derived carbon nanocomposite as a substitute for mercury in the catalytic hydrochlorination of acetylene, Nat. commun. DOI: 10.1038/ncomms4688.
29. J. Zhang, Z. He, W. Li, Y. Han, Deactivation mechanism of AuCl\textsubscript{3} catalyst in acetylene hydrochlorination reaction: a DFT study, RSC Adv. 2 (2014) 4814-4821.