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Ligand coordination approach for high reaction stability of an Au-Cu bimetallic carbon-based catalyst in acetylene hydrochlorination process

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The research and development of non-mercury catalyst for China’s PVC (poly vinyl chloride) industry is extremely urgent. Gold (Au) loaded on activated charcoal (AC), as a potential novel catalyst with high activity, has been regarded as an ideal substitution of mercury. However, the deactivation of gold catalyst caused by acetylene for long-term industrial application is a big challenge. In this work, a new methodology of ligand screening and design for gold catalysis was constructed. Trichloroisocyanuric acid (TCCA) was proved to be an excellent ligand. Besides, copper (Cu) was added and proved to be a favorable synergistic metal so that the content of Au in the catalyst could be further reduced to 0.2 wt% (weight percentage). Experimentally, the best ratio of each component was optimized to be Au:Cu:TCCA=1:5:20. The prepared 0.2 wt% Au catalyst had a conversion of over 98% with over 99% selectivity during 24 h operation under the temperature of 180 °C and GHSV (gas hourly space velocity) of 90 h⁻¹. Then over 6800 h pilot-trial has been carrying out to demonstrate its promising capability for practical application. Moreover, several characterization methods accompanied by DFT calculations were used, and it was proved that the high stability after TCCA introduction may come from its high ability of preventing high valence Au from reduction and inhibiting coking effect, and the electron interaction between Au and Cu could facilitate the dispersion of Au and lead to higher catalytic activity.

Introduction

Poly vinyl chloride (PVC) is a widely used synthetic resin material with the advantage of low cost, great mechanical strength, excellent flame retardance, good electrical insulation and high resistance of acids and bases.¹,² In 2013, the global demand of PVC reached 3.6×10⁷ t³. China is the world’s largest PVC production country, and its production capacity of PVC, which accounted for 48% in the world in 2010, has maintained a growth rate of 10% per year since 2003⁴. Currently, there are three main industrial processes for the production of vinyl chloride monomer (VCM), namely acetylene method, ethylene method and ethane method. Among these processes, acetylene method (also called calcium carbide method), relying on coal resources, has a strong advantage of cost, resource, technology and strategy in China. Annually, over 1.3×10⁷ t of VCM is produced by acetylene method in China, which occupies more than 70% share⁵. All these facts are testified by the data in Table S1. The core reaction of acetylene method is acetylene hydrochlorination reaction, namely the production of vinyl chloride by the single addition reaction between acetylene and hydrogen chloride. The equation with energy changes is as follows⁶:

\[ \text{CH≡CH} + \text{HCl} \xrightarrow{\text{Catalyst}} \text{CH}_2=\text{CHCl} \quad \Delta H = -124.8\text{ kJ·mol}^{-1} \quad (1) \]

This exothermic reaction was applied in industry as early as 1930s. Over the past years, the catalyst for this reaction was mercury chloride (HgCl₂) loaded on substrates, and the content of mercury was generally between 8 wt% (weight percentage) and 13 wt%. However, the shortcomings of this catalyst are distinct. Firstly, HgCl₂ is highly toxic and the LD₅₀ (50% lethal dose) of rat through mouth is 1 mg/kg. Furthermore, HgCl₂ volatilizes easily⁶, and the formation of hot spots over 200 °C in the fixed bed reactor due to exothermic effect exacerbates its volatilization, leading to severe mercury escape from the reactor during the reaction process. Although the downstream absorption device for mercury capture and recycling is always set up after the VCM synthesizer, a great deal of mercury still discharges into the environment. It is estimated that 8×10⁷ kg of HgCl₂ is consumed for PVC production in China per year, leading to a 2×10⁷ kg HgCl₂ loss which may cause severe human injury and environmental pollution⁷. Meanwhile, a depletion of mercury in China can be anticipated and hence the mercury resources in many famous mercury mines in China have been used up⁸. And this situation leads to increasing import and high mercury price, which brings new challenges for low value-added PVC industry⁹. More importantly, the mercury restriction of international organizations is becoming increasingly stringent.
On 19 January 2013, a legally valid protocol called Minamata Conviction was passed by the United Nations Environment Programme (UNEP), which established specific standards and restrictive measures for mercury utilization. To face this challenge, China has formulated a clear three-step plan for mercury elimination: low mercury stage in 2010-2015, mercury stabilization stage in 2015-2020 and comprehensive mercury prohibition stage from 2021. It can be clearly seen that the mercury based PVC industry in China has fell into deep crisis and the development of non-mercury catalyst is extremely urgent.

Since 1975, British researcher Hutching has devoted himself in exploring new active components for hydrochlorination reactions, and the strong regularity between the activity of metals in hydrochlorination and its standard electrode potential was established, and metals with a high electrode potential was anticipated to have a great hydrochlorination activity. Gold, with a standard electrode potential of $E^o(Au^{3+}/Au) = 1.42$ V, was selected as an ideal noble metal for these reactions. Besides, gold is stable, safe and clean, and the recycling cost can be greatly decreased since the loss of gold during reaction process is quite small. Based on these advantages, gold becomes feasible to act as a novel catalyst and has been widely studied these years. In 1991, Nkosi et al. prepared a catalyst with gold chloride (AuCl$_3$) as the active component and activated charcoal as the substrate. This catalyst performed a good activity under 1800 h$^{-1}$ GHSV (gas hourly space velocity, only 30 h$^{-1}$ needed for industry). In 1998, Thompson et al. compared the activity and stability of noble metals including gold, iridium, palladium, rhodium, ruthenium and platinum. It was observed that the deactivation rate was proportional to initial activity for many metals, but gold could demonstrate great activity while maintaining low deactivation rate, indicating its potential for practical application. In 2007, Conte et al. explored the mechanism and the impacts of reactants for hydrochlorination reaction. Experiments proved that HCl could activate the catalyst while acetylene could cause a rapid deactivation. Then, adding another noble metal (including Pt, Pt, Ir, Rh, Ru) was conducted to improve the catalytic property. However, although the addition of noble metals could alter the initial activity of the catalyst, an enhancement of stability was not observed. In 2010, Wang et al. studied Au-Cu bimetallic catalysts and found that Cu could decrease the content of Au in catalyst to a large extent without losing the activity, and thus the cost of catalyst could be further reduced. Then 100 h long-term experiment was operated under the temperature of 160 °C and the GHSV of 100 h$^{-1}$, and the 0.4 wt% gold catalyst maintained good performance. From 2012, Zhou et al. in our group performed a detailed work on Au-Bi and Au-Bi-Cu system, and the content of Au in catalyst was further reduced to 0.2 wt%. This catalyst could demonstrate a better activity and stability compared to 1 wt% Au-only catalyst. In 2014, Zhou et al. explored the methodology of adding ligands to enhance the stability of catalysts, and potassium thiocyanate (KSCN) was confirmed as an effective ligand to suppress the deactivation of Au$^{3+}$ reduction. Hence the stability of catalyst was enhanced significantly and a novel 0.25 wt% low Au content catalyst could demonstrate the same catalytic performance as the 10 wt% Hg industrial catalyst. By progressively scaling up, 3000 h pilot-trial analysis was accomplished and verified the long-term feasibility of the catalyst (Data were used to make comparison in Fig. 5).

Meanwhile, plenty of related patents emerged constantly these years. In 2008, N. A. Cathy et al. loaded gold nanoparticles on carbon materials with high specific surface areas, and the prepared 1 wt% Au content catalyst demonstrate the same catalytic properties as traditional mercury catalysts. In the same year, Jiang et al. prepared catalysts by combining AuCl$_3$ with some normal metal chlorides and loading them on AC, and catalysts with a gold content as low as 0.5 wt% were gained. These catalysts performed a conversion of 95~98% under 250 h$^{-1}$ GHSV. In 2010, Luo et al. combined gold chloride with other noble metals (including Pt, Ru, Rh and Pd) and normal metals (including Cu, Zn, K, Ba and Ni), and a catalyst adapted in fluidized bed reactor was designed. The catalyst with a gold content of 0.05 wt%~0.5 wt% could demonstrate a conversion of 85% under 400 h$^{-1}$ GHSV and the deactivated catalyst could be regenerated for reuse. In 2011, Li et al. impregnated coconut AC in the solution of silver and nickel nitrate was plated. Then, 0.4 wt% gold was loaded on the modified substrate and the catalyst performed 98% conversion under the GHSV of 640 h$^{-1}$. In the same year, Zhang et al. took gold together with cobalt and lanthanum as the active components, which were loaded on a variety of substrates such as activated charcoal, silica, silicon carbide and zeolite. Then, additive metals including potassium, sodium, bismuth, iron, nickel, copper and zinc was appended and the prepared 1 wt% Au content catalyst demonstrated 98.4% conversion under 360 h$^{-1}$ GHSV. In 2012, Zheng et al. adopted thiourea and thiocyanate as ligands and potassium, cobalt, copper and zinc as synergistic metals. 1 wt% gold content catalyst was evaluated and 92% conversion and 99% selectivity was observed under the GHSV of 360 h$^{-1}$. In 2013, Dai et al. modified AC by chemical vapor deposition method, and the raw gas was selected to be ammonia, melamine and urea. Then gold was loaded and the 0.2 wt% gold content catalyst performed 89% conversion under the GHSV of 360 h$^{-1}$. In the same year, several novel substrates such as N-doped carbon nanotubes, graphene and mesoporous carbon was applied by Zhou et al. in our group. The catalyst with 0.35 wt% gold content by our group could maintain a conversion of 80% under 600 h$^{-1}$ GHSV for a long time.

However, as for practical application, catalyst stability enhancement, especially in thousands of hours’ long term evaluation, is still scant due to the stringent requirements of industrial experiment and limited laboratory conditions. Nkosi classified the reason of deactivation into two types: coking effect and gold reduction, and this mechanism was accepted by many researchers. Unfortunately, the effective way to eliminate deactivation remains unsolved. However, stability
is a fatal factor for industrialization since a high stability not only guarantees good quality of products but also reduces additional operation and management cost by prolonging operation period. In general, catalysts running continuously for at least 8000 hours are always expected in industry. Therefore, a further stability enhancement of catalysts with maintained activity is still the most important work at present in this field.

This paper is exactly aimed on the new methodology of stability enhancement of gold catalysts for hydrochlorination. In this work, new ligands were tested and active components were tuned to create a better catalyst. Finally, catalysts with sufficient activity and high stability were prepared and some factors enhancing stability were further studied.

**Experimental**

**Pretreatment of activated carbon (AC)**

Specific surface area, pore volume and intensity should be considered comprehensively during the selection of AC. In this work, coconut shell activated charcoal with a size of 50~200 mesh, a specific surface area of 600~800 m²/g was selected as substrate. First, AC was soaked in 6 mol/L hydrochloric acid (AR, Beijing Chemical Works) for 24 h. Then deionized water was used to rinse the substrate until pH=7. Finaly, AC was dried under 100 °C for 24 h and stored for later use.

**Screening of anionic ligands**

It has been repeatedly confirmed that gold in high valence (+3 or +1) rather than valence zero has a better activity on hydrochlorination reactions. During the reaction, acetylene tends to reduce gold to zero valence and the activity decreases correspondingly. Furthermore, metallic gold tends to agglomerate on the surface of the catalyst and leads to further deactivation. So the main purpose of introducing ligand is to stabilize gold at high valence so that reduction deactivation can be inhibited. As for the complexation effect, there is a more conspicuous specificity for gold than other metals. According to the theory proposed by Bond et al., gold is located in the sixth period, where lanthanide contraction significantly affects the distribution of electron cloud, leading to a result that the peripheral electrons of gold contract dramatically so that the atom radius of gold is even smaller than that of silver in the fifth period and the same group, leading to a high electron cloud density. Meanwhile, numerous extranuclear electrons and orbitals surround gold atoms. Therefore, the charge distribution is of great importance for the stability of gold complexes. It was reported in literature that if a single  \( \sigma-\sigma \) coordinate bond is formed between gold ion and the ligand, the bond strength is not sufficient and negative charge will accumulate in center gold ion due to electron transfer, leading to a poor stability of the complex. However, if low energy unoccupied \( \pi \) orbitals existed in the ligand, negative charge will partially return from the center ion to these orbitals. This effect, which could be called \( \sigma-\pi \) feedback effect, not only strengthens the bond, but also balances the charge between center gold ion and the ligand, and thus stabilizes the complex. For instance, there are no low energy unoccupied orbitals in \( \text{H}_2\text{O}, \text{F}^-, \text{NH}_3 \), so they fail to form stable complexes with gold despite that they are the most common ligands. On the contrary, \( \text{Cl}^-, \text{CN}^- \), thiourea and malononitrile become ideal ligands for gold due to the existence of such orbitals and they are widely used in gold leaching process. Besides, the electrophilic effect of coordination atoms and neighbor atoms can make contributions to the balance of charges and thus improve the stability of complexes. In general, the existence of chloride, bromide, oxygen and sulfur atoms can intensify this effect. According to above analysis and previous work in our group, it can be speculated that ligands containing sulfur atom or nitrogen conjugated system could strongly coordinate with gold ions.

According to the previous theoretical analysis, a new exploration of these ligands was carried out in this work. However, there were still a plenty of ligands and a further screening was required. High complexation ability, high stability, structure simplicity, low toxicity and low cost were taken into consideration during the screening process.

Finally, with reference to the ligands reported in literatures and patents, sodium thiosulfate (\( \text{Na}_2\text{S}_2\text{O}_3 \)), melamine, cyanuric acid (CA) and trichloroisocyanuric acid (TCCA) were selected. The structures of these ligands were shown in Chart 1.

To give a further analysis of these ligands, we could concluded that: (1) \( \text{Na}_2\text{S}_2\text{O}_3 \) has a sulfur atom and three oxygen atoms which could act as coordination atoms, but no conjugated system was formed; (2) CA has not only a conjugated system but also three oxygen atoms which provide intense electrophilic effect; (3) melamine has a well-constructed conjugated system, but the electrophilic effect of nitrogen atoms is not very strong; (4) TCCA has three more highly electrophilic chloride atoms than CA. Then, it can be concluded that the extent of fulfilling the requirement mentioned above for these four ligands is in the following order: \( \text{Na}_2\text{S}_2\text{O}_3<\text{CA}<\text{TCCA} \).

**Load of active components**

Incipient impregnation method was used to prepare catalysts. First, chlorauric acid (\( \text{HAuCl}_4 \)) was added. Then dilution procedure was performed, and finally AC was dried under 105 °C and stored for later use.

**Reaction evaluation of the catalyst**

Fig. S1 is the diagram for the lab-scale evaluation equipment. The evaluation procedure was as follows: First, 2,0000 g catalyst was added into U-shaped silica tube with a diameter of 6 mm and put in the furnace. Then \( \text{N}_2 \) (99.999%, Beijing Beiwen Gas Works) was fed continuously at 180 °C to further
desiccate the catalyst. Next, HCl (99.9%, Beijing Beiwen Gas Works) was fed to activate the catalyst for 30 min. Finally, acetylene (99.99%, Beijing Fuxingrui Industrial Gas Co., Ltd.) was fed and a volume ratio of HCl:C$_2$H$_2$=1.1:1 was maintained during the evaluation. Gas chromatography (GC, SP-3420, Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd., flame ionization detector) was used to determine the conversion of acetylene and the selectivity of VCM. Samples were collected and tested every 15 minutes. The typical chromatogram was shown in Fig. S2. Only one impurity peak appeared in the diagram and it was identified to be acetone which came from the cylinder of acetylene source gas, indicating the excellent selectivity of VCM.

(A) 2Na$^+$-O-S-O-O$^-$ (B) NH$_2$(NH$_2$)$\text{N}$ (C) O-H-N$\text{N}$O (D) O-N-Cl$\text{N}$O

**Chart 1.** Structure of (a) Na$_2$S$_2$O$_3$, (b) melamine, (c) CA, (d) TCCA.

**Characterization**

XRD (X-ray diffraction) was carried out on DB ADVANCE Rigaku D/max-RB diffractometer, Bruker, Germany. Radiation source was Cu $K_{\alpha}$, tube voltage 40 kV, tube current 20 mA. TEM (transmission electron microscope) was performed by JSM 2010, JEOL, Japan. Operation voltage was 200 kV. TPR (temperature programmed reduction) analysis was carried out on an ASAP 2920 instrument (Micrometrics Instrument Corporation, USA) equipped with a thermal conductivity detector (TCD). XPS (X-ray photoelectron spectroscopy) was analyzed by PHI Quantera SXM Energy dispersive spectroscopy, ULVAS-PHL. INC., Japan. Binding energy was calibrated by C 1s peak (284.6 eV). ICP-AES (inductively coupled plasma atomic emission spectrometer) was carried out on an IRIS Intrepid II XSP equipment. For measuring the content of metals, a certain amount of catalyst was calcined at 600 °C for 2 h and the rest was dissolve in aqua regia to form an aqueous solution. The Brunauer–Emmett–Teller (BET) specified surface area was measured by Ar adsorption/desorption at liquid Ar temperature using an Autosorb-iQ2-MP-C system. Before measurements, the sample was degassed at 30 °C. DFT (density functional theory) calculation was operated by Gaussian 09 software. B3LYP functional was used for optimization and energy calculation. 6-31G(d) electron basis set was set for all atoms except Au, for which Lanl2dz was adopted. The energies were calculated at room temperature (298.15 K) and the pressure of 1 atm.

**Results and discussion**

**Comparison among different ligands**

First, high GHSV 600 h$^{-1}$ was adopted to give a preliminary evaluation and comparison among different catalysts prepared by adding different ligands. The Au content was kept constantly at 0.25 wt% and the mole ratio of Au to ligand was kept as 1:2. Results were shown in Fig. 1. It can be seen that gold itself demonstrated a certain activity under high GHSV, but the stability remained to be improved. The activity and stability of catalyst with Na$_2$S$_2$O$_3$ ligand was undesirable, and it should be excluded from this reaction system. CA could partially enhance the stability of the catalyst but the activity was also negatively affected. As for melamine ligand, an activation stage appeared but the final stage stability was undesirable. Besides coking effect, the lability of Au-Melamine structure could be the factor of poor stability. However, when TCCA was added, the stability was significantly increased while no notable effect on initial activity was observed. This result showed that Au and TCCA could gradually form a stable structure, and the reduction effect could be inhibited to a large extent. It should be emphasized that this high stability was meaningful for industrial application.

![Fig. 1. Performance of 0.25 wt% Au catalysts with different ligands, reaction conditions: T=180 °C, GHSV=600 h$^{-1}$, mole ratio of Au to ligand in all catalysts was 1:20.](image)

It should be noted that the order of stabilization effect of these ligands was exactly the same as mentioned before, confirming the rationality of our ligand selection strategy.

**Optimization of the ratio between Au and ligands**

After the best ligand TCCA was determined, an optimization of the ratio between Au and TCCA was carried out. Results were shown in Fig. 2. It can be concluded that neither an excessive nor an insufficient content of TCCA in the catalyst led to good activity and stability, and mole ratio Au:TCCA=1:20 could be the optimum. On one hand, the catalyst with Au:TCCA=1:8 performed similar initial activity with that of the catalyst with Au:TCCA=1:20, but the initial activity of catalyst with Au:TCCA=1:40 decreased for 5%. This phenomenon told us that mechanisms of poor performance in high TCCA and low TCCA content catalysts were different. The poor stability of Au:TCCA=1:8 catalyst could be attributed to the failure that
significant ligand could not provide a full protection of gold ions. This assumption could be confirmed by comparing the reaction performance of Au:TCCA=1:0 (no ligand, in Fig. 1), Au:TCCA=1:8 and Au:TCCA=1:20 catalysts. On the other hand, the reason of decreased activity and stability of Au:TCCA=1:40 catalyst could be that the excessive TCCA covered some active sites of gold nanoparticles. These judgments were further proved by SEM images in Fig. S5. From these images, we could found that without ligand, Au was unevenly distributed on the AC substrate and severe agglomeration of >100 nm particles could be found, leading to poor catalytic performance (Fig. S5(a)). In the catalyst with Au:TCCA=1:8, the distribution of Au was significantly improved, but several large Au particles could still be seen (Fig. S5(b)). As for Au:TCCA=1:20 catalyst, the distribution of Au was further improved, only small gold particles could be found and the amount of visible particles at micrometer scale was significantly reduced (Fig. S5(c)). However, when the ratio of Au:TCCA enhanced to be 1:40, excessive TCCA could crystalize on the surface of AC substrate, which could be clearly seen in the SEM image (Fig. S5(d)). These salts could partially cover Au active sites, leading to poor catalytic activity.

Addition of synergistic metal Cu

It could be seen from Fig. 1 that although TCCA was confirmed to have an excellent stabilization effect for Au, the activity of the catalyst was not high enough for practical application. Therefore, to further enhance the activity for this catalyst so that Au content could be maintained to a low level, the addition of synergistic metal Cu was taken into consideration. Results were shown in Fig. 3 and the mole ratio of Au to Cu was fixed to 1:20. It could be seen that when the ratio of Au:Cu changed from 1:0 to 1:5, a significant enhancement of activity was observed. However, as the content of Cu increased, the stability of the catalyst reduced correspondingly. This phenomenon told us that an inconsistency between high activity and good stability should be balanced. Since the further increase of Cu content from Au:Cu=1:5 to 1:10 could not provide significant increase on activity, Au:Cu=1:1~1:5 was the reasonable ratio.

Long-term experiment

To verify the practical feasibility of the novel Au/Cu/TCCA catalyst, a long-term experiment was carried out under 90 h⁻¹ GHSV. Results were shown in Fig. 4(a). The catalyst with a gold content of 0.2 wt% maintained a conversion of over 98% during 24 h, and the deactivation rate was calculated to be 0.0225% conversion•h⁻¹, which was lower than half of that in 0.25 wt% Au/Cu/KSCN system (deactivation rate 0.0478% conversion•h⁻¹) in our previous work, despite that the latter was operated at a lower GHSV of 60 h⁻¹. Because of the good performance, this catalyst was loaded on pilot-trial equipment. A single tube fixed bed reactor with 80 mm inner diameter was used and 2.5 kg catalyst was loaded. Then, the source gas for industrial production was directly fed to the tube for a long-term evaluation and the result was compared with Au/Cu/KSCN system in Fig. 4(b). It could be clearly seen that the novel catalyst had better stability although the Au content was lower. According to the trend of conversion variation during 6800 h, it could be expected that the novel catalyst could be run for over 8000 h, fulfilling the requirement for industrialization.

Characterization

After gaining the promising result, several characterization methods were carried out in order to explore the factors
affecting activity and selectivity resulted from ligand and metal introduction.

**TEM**

TEM was further used to observe gold particle size in fresh and spent Au/TCCA and Au catalysts without ligands. Results were shown in Fig. 5. The average gold particle size was 2.9 nm for fresh Au/TCCA catalyst, and gold particles in this size range were confirmed to be very active. While for fresh Au catalyst without ligands, the average size was 45.7 nm, indicating significant agglomeration. The assistance of dispersion by adding TCCA ligand was confirmed. After reaction, the spent Au/TCCA catalyst maintained an average gold particle size of 7.6 nm, while for Au catalyst without ligands this value reached 61.1 nm. Since the activity of agglomerated gold particles became much lower, the protection of small particles could lead to maintained activity, namely, a good stability.

**XRD**

The XRD spectra were carried out to confirm the dispersion of gold particles on the substrate, gold with no ligand was used for comparison. The results were shown in Fig. 6. As expected, Au loaded on AC with no ligand (a) demonstrated obvious characteristic peak of metallic Au. For Au/TCCA system (b and c), both the fresh and spent catalyst showed no peak except the wide peak of carbon substrate. Besides, the addition of Cu would not lead to the appearance of new peaks (d and e). The failure of observing peaks could be caused by the low gold content adding up to relatively small particle size. The improvement of gold particle dispersion by TCCA introduction was reconfirmed.

**Fig. 5.** TEM images and gold particle size statistics of (a) Au/TCCA, fresh, (b) Au/TCCA, spent, (c) Au, no ligand, fresh, (d) Au, no ligand, spent catalysts. Au content 0.25 wt%, mole ratio of Au to ligand was fixed to 1:20. Inlet diagrams illustrated the particle size distribution in each catalyst. Average diameter and standard deviation were also given in the diagram.

**Fig. 6.** XRD spectrum of Au catalyst with no ligand, Au/TCCA catalysts and Au/Cu/TCCA catalysts. (a) Au, no ligand, (b) Au/TCCA, fresh, (c) Au/TCCA, spent, (d) Au/Cu/TCCA, fresh, (e) Au/Cu/TCCA, spent. Au content 0.25 wt%.

**TPR**

TPR was used to evaluate the reducibility of Au in catalysts and the results were shown in Fig. 7. It could be clearly seen that a strong characteristic peak for carbon substrate was found at 680 °C (blue line). After Au was loaded, a characteristic reduction peak at 370 °C was found (black line). TCCA ligand itself could introduce a weak peak located at 350 °C (magenta line). However, when TCCA was introduced to Au catalyst, the intensity of Au reduction peak was significantly enhanced, indicating more reducible Au species was formed (red line). The reason could be that the enhancement of Au nanoparticle dispersion caused by TCCA led to more Au atoms at high valence and these Au species could be stabilized by TCCA. After Cu was introduced, not only a distinct peak of Cu at 460 °C was found, but also the intensity of Au reduction peak was increased, proving that Cu could interact with Au so that more reducible Au species was formed (green line). These Au atoms at high valence led to the enhanced activity of the catalyst.

**Fig. 7.** TPR results of Au catalysts with different ligands. Au content: 0.25 wt%, evaluation condition: $V(H_2)=100 \text{ mL/min}$, heating rate 10 K/min.

**XPS**

XPS analysis was carried out to detect the valence state of gold before and after reaction. According to literature and...
calibration, the binding energy of Au(III)\(4f_{7/2}\), Au(I)\(4f_{7/2}\) and Au(0)\(4f_{7/2}\) was confirmed to be located at 89.8 eV, 88.2 eV and 87.8 eV. And those of Au(III)\(4f_{7/2}\), Au(I)\(4f_{7/2}\) and Au(0)\(4f_{7/2}\) was located at 86.4 eV, 85.1 eV and 84.2 eV. The XPS spectra of fresh and spent catalysts of Au system without ligand and Au/TCCA system were shown in Fig. 8. It should be noted that in order to obtain distinct peaks, 0.5 wt% higher Au content was adopted. By comparison, it could be found that Au and Au/TCCA experienced different reaction mechanisms. As for Au without ligand system, there was a strong peak of Au(III) in the spectrum of fresh catalyst, indicating the existence of abundant gold in +3 valence, which led to a high initial activity. However, as the reaction going on, the peak of Au(III) gradually disappeared, and the activity decreased accordingly. But for Au/TCCA system, the main state of gold in fresh catalyst was +1 valence and zero valence, but after reaction, the peak of Au(III) gradually formed. This result indicated that there was an activation process in Au/TCCA system to form highly stable structures where gold was in +3 valence. These structures were crucial for the maintained activity in the catalyst, and the activation process was crucial for the catalyst to have a long-term stability.

In order to explore the effect of Cu addition in Au/TCCA system, XPS analysis of Au/Cu/TCCA catalyst was conducted and results were shown in Fig. S3. The spectrum of Au/Cu/TCCA system was similar to that of Au/TCCA system: most of gold stayed in +1 valence and zero valence in fresh catalyst, and gold in +3 valence generated after reaction. This spectrum again illustrated that an activation process to form highly stable structures was taken place in Au/TCCA system, and the addition of Cu had no notable influence on this process. It could be also deduced that the reduction deactivation was not the main reason for decreased stability of Au/Cu/TCCA system, coking effect introduced by Cu may be predominant.

**Fig. 8.** (a) XPS spectrum for Au, no ligand system, Au content 0.5wt%, (b) XPS spectrum for Au/TCCA system, Au content 0.5wt%, Au:TCCA=1:20 (mole ratio).

**ICP-AES**

ICP-AES was used to determine the content of metal in these catalysts. Results was shown in Table 1, the result given by XPS was also listed for comparison. It could be seen that the Au content of all the catalysts given by ICP measurement was consistent with the calculated one, indicating that little Au was lost during the reaction and calcination process. Therefore, the stability of Au in these catalysts was confirmed. However, the Au content measured by XPS was relatively lower. Since XPS mainly measured the content of elements on the surface, this phenomena could be due to that Au preferred to be loaded on the inner surface of AC substrates. As for Cu, XPS data told us that Cu was almost uniformly distributed on AC substrates, The relatively lower results derived by ICP test could be attributed to the loss of Cu during the calcination process.

**BET**

BET test was constructed to explore the morphology of catalysts. A typical adsorption/desorption isotherm was shown in Fig. S4 and a typical IV type hysteresis loop could be found. The results derived from DFT method were shown in Table 2. It could be seen that after the catalyst was used, a decrease of specific surface area and pore volume along with an increase of average pore diameter was observed, indicating coke was formed and blocked in the microscopic pores of catalysts. It should be noted that the specific surface area and pore volume in Au/TCCA/AC decreased by 12.4% and 5.07% respectively. While when Cu was added, these two values changed to be 34.1% and 14.9%, proving that the addition of Cu could cause severe coking effect and the stability of catalyst was therefore negatively affected.

**Table 1.** Metal content derived from ICP and XPS measurement

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<th>Sample</th>
<th>Method</th>
<th>Au</th>
<th>Cu</th>
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<td>-</td>
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<tr>
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<td>ICP</td>
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<td>-</td>
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<td>XPS</td>
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<td>-</td>
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<tr>
<td>Au/Cu/TCCA/AC, spent</td>
<td>XPS</td>
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<td>-</td>
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</table>

**Table 2.** BET analysis results for Au/TCCA catalysts, Au content 0.25 wt%, Au:TCCA=1:20 for all catalysts and Au:Cu=1:5 (mole ratio) for Au/Cu/TCCA catalysts

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<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TCCA/AC, fresh</td>
<td>855.5</td>
<td>0.947</td>
<td>1.99</td>
</tr>
<tr>
<td>Au/TCCA/AC, spent</td>
<td>748.7</td>
<td>0.899</td>
<td>2.37</td>
</tr>
<tr>
<td>Au/Cu/TCCA/AC, fresh</td>
<td>768.9</td>
<td>0.926</td>
<td>1.89</td>
</tr>
<tr>
<td>Au/Cu/TCCA/AC, spent</td>
<td>596.4</td>
<td>0.788</td>
<td>2.05</td>
</tr>
</tbody>
</table>

**Mechanism hypothesis and DFT calculation results**
Upon abundant experiment data and characterization results, two aspects should be taken into consideration in order to improve the carbon-based gold catalysts by adding ligands. On one hand, the dispersion of gold nanoparticles influenced by ligands is crucial for maintaining activity. On the other hand, the formation of stable structures resistant to reduction between gold and ligands could enhance the stability.

Concerning the dispersion of gold nanoparticles, solvent type, the acidity of solution, the solubility of complexes and the preparation method are all of great importance. As for the stabilization effect, the electronic structure of ligands deserves prime attention. DFT calculation was carried out for Au system with or without ligand addition and the calculated energy for each optimized species was listed in Table S2. For easier comparison, the energies of reactant were artificially set to be 0, and the energy for acetylene adsorption for each system was listed for comparison in Fig. 9. It can be seen that the existence of conjugated structure and electrophilic group in TCCA could lead to an electron feedback from active Au atom. Then, the accumulated electron cloud density could be balanced and the interaction between Au and acetylene could be weakened, leading to a negative adsorption energy (-570.35 kJ/mol) which could preventing the reduction of Au\textsuperscript{3+} by acetylene and the side reaction caused by acetylene polymerization. As for Au/CA and Au/Melamine systems, it could be found that the adsorption energies of acetylene in Au/CA and Au/Melamine systems were 182.68 and 139.25 kJ/mol, respectively, which were much higher than that of Au/TCCA (-570.35 kJ/mol). Therefore, these ligands could not weaken the interaction between acetylene and Au species as TCCA could, so the stability of these catalysts was not as good as Au/TCCA catalyst. Furthermore, the poor performance of Au/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} could be due to the agglomeration effect caused by the decomposition of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (some Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} formed element S under acidic environment), which could be seen in SEM images in Fig. S6. Therefore, TCCA could be a better stabilizer for Au catalysts than the other ligands mentioned in this work. Since the reduction of Au\textsuperscript{3+} and coking effect caused by acetylene deposition are two main facts for deactivation, the importance of inhibiting these two factors for catalyst stabilization was fully confirmed in this passage. Thus, a reasonable criteria of ligand screening for gold dispersion and stabilization on active substrates were successfully constructed here and will be helpful for future studies, which may be extended to other reactions catalyzed by gold.

Furthermore, Cu was selected as a synergistic metal to enhance the activity of gold catalyst. Cu could facilitate the dispersion of gold nanoparticles and hence enhance the activity. However, it could also demonstrate an adverse effect on the stability of the catalyst due to coking effect. Therefore, an optimization of the ratios of active components in the multi-component intricate system was of great importance.

Fig. 9. Illustration and DFT calculation for Au systems. (a)Au system, (b)Au/TCCA system, (c)Au/CA system, (d)Au/Melamine system. Yellow balls for Au atoms, green for Cl, grey for C, blue for N, red for O and white for H.

Comparison with other published results

Comparison of stability and activity among different catalysts was demonstrated in Fig. 10 and corresponding information were listed in Table 3. The activity was calculated on the base of TOF (turnover number) and the stability was evaluated by the estimated time of 1% conversion decrease. It could be seen that in this work novel catalysts with both excellent activity and stability was prepared, indicating its great potential for industrial application.

Conclusions

Efforts were made to significantly enhance the stability of carbon-based gold catalyst for acetylene hydrochlorination while maintaining high activity. This purpose was realized by adding TCCA as the ligand for enhancing stability and Cu as the synergistic metal for enhancing activity. The highest TOF of these catalysts reached 1.01 s\textsuperscript{-1} with an excellent stability. Laboratory and over 6800 h industrial evaluation was operated to verify the practical feasibility of the 0.2 wt% low gold content catalyst, and characterization was carried out to reveal the factors influencing activity and stability. The acceptable cost and great performance of this catalyst may promote the development of green and effective non-mercury catalysts in China’s PVC industry.
of 600 h \(^{-1}\) hydrochlorination catalysts, only those data with a GHSV range of 5-1000 h \(^{-1}\) were selected. References: Nkosi 49, Hutchings 40, Conte 18, Zhou 23, 24, 47, Wang 50. More information of these catalysts were listed in Table 3.

Table 3. Information of different catalysts in Fig.10.

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Year</th>
<th>Au content (wt%)</th>
<th>GHSV (h (^{-1}))</th>
<th>(\text{V(C}_2\text{H}_4\text{): V(HCl)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nkosi</td>
<td>1991</td>
<td>1</td>
<td>1080</td>
<td>-</td>
</tr>
<tr>
<td>Conte(1,2,3)</td>
<td>2007</td>
<td>1</td>
<td>870</td>
<td>1:1</td>
</tr>
<tr>
<td>Hutchings</td>
<td>2009</td>
<td>1</td>
<td>1080</td>
<td>-</td>
</tr>
<tr>
<td>Zhou(1)</td>
<td>2009</td>
<td>0.5</td>
<td>600</td>
<td>1:1</td>
</tr>
<tr>
<td>Wang</td>
<td>2010</td>
<td>0.5-1</td>
<td>1200</td>
<td>1:1.2</td>
</tr>
<tr>
<td>Zhou(2)</td>
<td>2012</td>
<td>0.3</td>
<td>600</td>
<td>1:1.1</td>
</tr>
<tr>
<td>Zhou(3)</td>
<td>2014</td>
<td>0.3</td>
<td>1200</td>
<td>1:1.1</td>
</tr>
<tr>
<td>This work(1)</td>
<td>2014</td>
<td>0.25</td>
<td>600</td>
<td>1:1.1</td>
</tr>
<tr>
<td>This work(2)</td>
<td>2014</td>
<td>0.2</td>
<td>600</td>
<td>1:1.1</td>
</tr>
</tbody>
</table>

Acknowledgments

This work was supported by the National 863 Research Program of China (863 Program, 2012AA062901), and the Ministry of Science and Technology of China (2008BA41B02).

Thanks for the valuable discussion and comments from Prof. WEI Fei, Prof. WANG Jinfu and Associate Prof. ZHANG Qiang in the Beijing Key Laboratory of Green Reaction Engineering and Technology. Thanks for the assistance on DFT calculation from Associate Prof. LU Diannan in the Department of Chemical Engineering, Tsinghua University and Prof. ZHONG Chongli, Associate Prof. YANG Qingyuan from Beijing University of Chemical Technology.

Notes and references

2. X. Cui, Jiangsu Chlor-Alkali, 2008, 15-25.
A novel high stability gold catalyst for acetylene hydrochlorination was designed and prepared by adding trichloroisocyanuric acid (TCCA) as a ligand and Cu as the synergistic metal, which can promote the development of non-mercury catalysis for China’s PVC industry.