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The Au-Cu bimetal catalyst by renewable γ-Al_2O_3 as support for acetylene hydrochlorination

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Abstract

Bimetal catalyst $AuCl_3$-$CuCl_2$ was prepared by several different γ-Al_2O_3 supports and the catalytic properties towards acetylene hydrochlorination were assessed in a fixed-bed reactor. The comparison indicated that one of the catalysts attained the highest activity with the C_2H_2 conversion of 97%, which was far more than the others. Catalysts were characterized by detailed XRD, N_2-BET, NH_3-TPD，FT-IR and CO_2-TPD analysis. It proposed that the base site contributed to its high catalyst activity compared with the others, instead of the acid site or the textural properties on the support, the activity and the life of the catalysts can be improved significantly by treating the supports with KOH. In addition, the results of N_2-BET, TGA and SEM indicated that the catalysts deactivated rapidly due to the carbon deposition, and the actual amount of coke deposition was 18.0% after the reaction.$AuCl_3$-$CuCl_2$/γ-Al_2O_3 was easy to regenerate for the catalyst by burning off in the air atmosphere for 10 min. The activity of the regenerated catalyst could nearly reach to the level of fresh catalyst.

Keywords: Acetylene hydrochlorination; Support; Al_2O_3; Base site; Regeneration

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1. Introduction

Vinyl chloride monomer (VCM) is mainly used for synthesis of polyvinyl chloride (PVC) which is widely used in every aspect of life.[1] In China, about 70% of vinyl chloride monomer products are produced from the acetylene hydrochlorination which is based on the catalyst of $HgCl_2$ supported on the activity carbon.[2, 3] However, the toxicity and volatility of the $HgCl_2$ can cause serious troubles to the environment and human beings' health, which has been driven many researchers to study non-mercuric catalytic systems. Nowadays, Au had been known as an efficient catalyst metal.[4, 5] M. Conte [6, 7] studied the gold catalyst in detail and found that gold had high activity in the acetylene hydrochlorination reaction. Its initial activity was higher than $HgCl_2$ catalyst. Alloying Au with other base metal was a promising way to improve the catalytic activity and a bimetallic Au-Cu/AC catalyst showed promising catalytic activity and an acetylene conversion of 99.5% at 200 h.[8] Au-based catalyst had drawn many researchers' attention, however, most of them were focused on activity carbon as the support which has low mechanical strength and poor regeneration capacity.[9] In normal practice, the Au dosage was more than 1% of the carbon support, which maked the catalyst too expensive for large scale use. This prompted us to consider whether there was a better support for acetylene hydrochlorination other than the activated carbon. While according to reports, Au base catalyst had very low activity when taking TiO_2 or SiO_2 as the support.[10]

In our previous work, we had demonstrated that bimetal Au-Cu catalyst had superior activities and longer lifetimes compared with the industrially preferred catalyst, which is based on carbon supported mercuric chloride.[8] Efforts also have been undertaken to explore Al_2O_3 as non-mercury catalysts support to reduce Au content for acetylene hydrochlorination.[11] In addition, it was found that the oxygen-containing groups, especially for the hydroxyl groups, the activity carbon played an important role in the high activity and excellent stability of Au-Cu/AC catalyst.[13] Due to the lack of mesopores and macropores in the carbon, the $HAuCl_4$ solution with the sizes of the 40~200 nm $AuCl_3$ particles[12], cannot diffuse into the inner part effectively, which will inevitably lead to aggregation of the $AuCl_3$ particles on the surface and also in the outer shell of the activated carbon pellets. The fact that Au^{3+} absorbed on the mesoporous of the activity carbon is the main activity site while the microporeone can be ignored to improve the usage of Au in some sense.[12] Meanwhile, the discontinuous distribution and disposable activity were its major shortcomings. All above facts prompted us to consider whether the γ-Al_2O_3, which was of mesoporous (20~50 nm) structure and contained abundant hydroxyl groups on the surface, could be an efficient support for Au-base catalyst in acetylene hydrochlorination. Currently, γ-Al_2O_3 was used as the support of preparing Au base catalyst for CO oxidation[14, 15]and hydrodechlorination of CCl_4.[16] However, as far as we were concerned, there were only a few literatures[11, 12] had reported the Au-base catalyst that supported on γ-Al_2O_3, and there was still much room to improve.

In this work, the γ-Al_2O_3 was employed as the support in $AuCl_3$-$CuCl_2$ catalyst for acetylene hydrochlorination. Because of its mesoporous structure, $AuCl_3$-$CuCl_2$ with the support of on γ-Al_2O_3 can effectively reduce the content of Au component. It was found that some γ-Al_2O_3 contain some special characters, they can be efficient supports for the catalyst. The possible mechanisms accounting for the enhanced stability and catalytic efficiency were also discussed. Effects of texture properties and base/acid site of γ-Al_2O_3 support to the catalyst activity were also analyzed in detail. In addition, the deactivation reason and the regeneration method were also investigated.

2. Experimental section

2.1 Catalyst preparation

Bimetallic Au–Cu/γ-Al_2O_3 catalysts were prepared using an incipient wetness impregnation technique.[8] γ-Al_2O_3 (A, B, C, D) from different companies (10 g, HengXin, YuanHeng, Hong Xing and BaoLai CO. LTD, China) were initially washed with dilute aqueous HCl (1 mol/l) at 25 ℃ for 1 h to remove the impurities on the surface, and prepared by impregnating $HAuCl_4$•$4H_2O$ (the content of Au assay 49.7%) aqua regia solution (1 g $HAuCl_4$•$4H_2O$/100 ml) 2 ml and $CuCl_2$•$2H_2O$ solution (6.25 g $CuCl_2$•$2H_2O$/500 ml) 20 ml, stirring for 3 h at 353 K, then dried at 423 K for 12 h.

The catalysts prepared by different supports were donated as ACAlA, ACAlB, ACAlC, ACAlD, respectively. Some of catalysts were named MACAlB, namely B pretreated with KOH donated as MB and the catalysts were prepared based on the process described elsewhere[8], in order to distinguish the effect of basic sites.

2.2 Catalyst characterization

BET surface area analysis and the pore size distribution were performed by obtaining nitrogen adsorption isotherms at 77 K in a Micromeritics ASAP2020 instrument. Temperature programmed analysis （including CO_2-TPD and NH_3-TPD） was performed by using a Micromeritic ASAP 2920 instrument, using 10% CO_2 (or NH_3) in argon (flow 50 ml/min, holding for 30 min) as an adsorption gas and a temperature ramp from 50 to 700 ℃(ramp rate, 10 ℃/min) when adsorbing. The morphology of the samples was examined by scanning electron microscope (SEM) (NOVA NanoSEM450, FEI Company, Holland). XRD data was collected by using a Bruker D8 advanced X-ray diffract meter with Cu-Kα irradiation at 40 kV and 40 mA in the scanning range from 10° to 80°. H_2-TPR was performed using a Micromeritic ASAP 2920 instrument, using 10% H_2 in argon (flow 50 ml/min) as a reductive gas and a temperature ramp of 50 to 600 ℃(ramp rate, 10 ℃/min) with the TCD detector recording the signal. IR spectra were obtained using Thermofisher Nicolet 6700 FT-IR spectrometer. XPS data was collected using an Axis Ultra spectrometer with a monochromatized Al-Kα X-ray source, a minimum energy resolution of 0.48 eV (Ag $3d_{5/2}$).

2.3 Catalyst testing

The catalytic performance in acetylene hydrochlorination was evaluated in a fixed-bed microreactor (diameter 10 mm) operating at the pressure of 0.1 MPa and temperature of 150 ℃. The reactor was purged with nitrogen to remove water in the reaction system before the reaction occured. Hydrogen chloride passed through the reactor at a flow rate of 50 ml/min for 2 h to activate the catalyst. After the reactor was heated to 150 ℃, acetylene (20 ml/min) and hydrogen chloride (22 ml/min) were fed through the heated reactor which contained 10 ml catalyst. The reaction product was analyzed by gas chromatography (GC-920, Al_2O_3 PLOT column). The catalyst activity is determined by the conversion of acetylene (X_{C2H2}) and selectivity of VCM (S_{VCM}), which are defined as:

$$X_{C2H2}= (1-\Phi_{C2H2}) \times 100\% \qquad (1)$$

$$S_{VCM}=\Phi_{VCM}/ (1-\Phi_{C2H2}) \times 100\% \qquad (2)$$

Of which Φ_{C2H2} is residual volume fraction of acetylene and Φ_{VCM} is volume fraction of chloroethylene.

3. Results and discussion

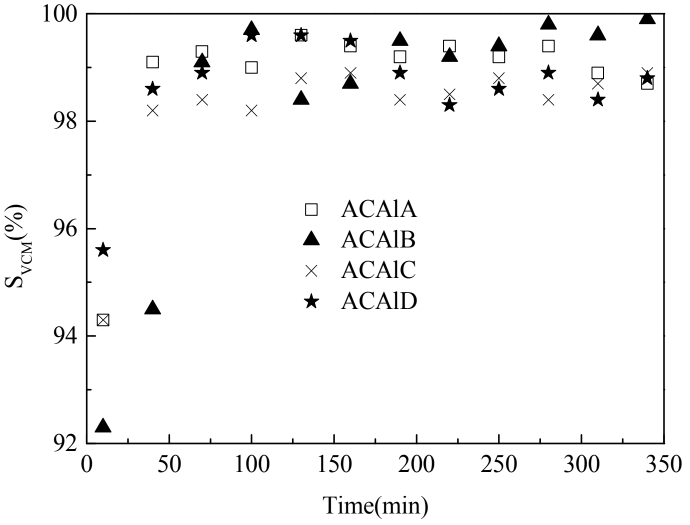
3.1 Catalytic activity

Catalysts with different supports were conducted in a fixed bed reactor to their catalytic performance in acetylene hydrochlorination. The X_{C2H2} and S_{VCM} with reaction time are illustrated in Fig. 1. It showed that all the catalysts had excellent selectivity toward C_2H_3Cl (Fig. 1a). However, their activities were quite different (Fig.

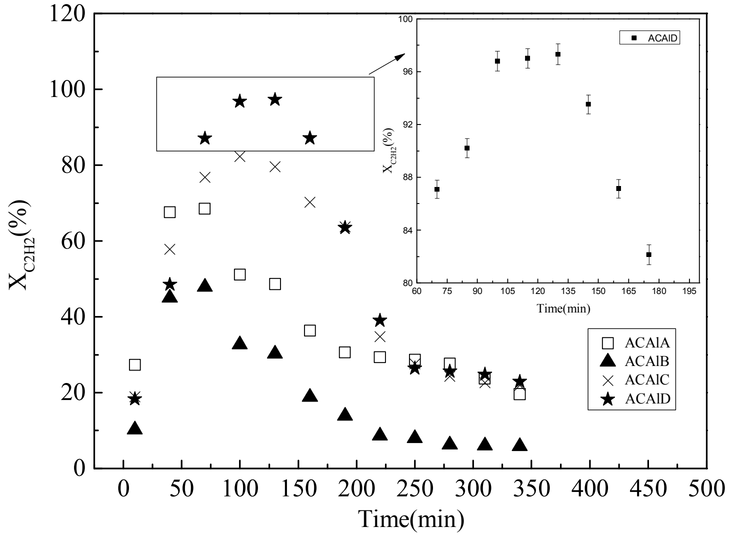
1b). It showed that catalysts performed a growing trend in previous time, and decreased after running for 2 h. ACAlD had the best performance among the samples with a highest conversion of 96% and stabilization about 90%. For compared, three other catalysts have the conversion from 40% to 80%, which were significantly lower.

The ACAlD had the highest C_2H_2 conversion which was contrary to its minimum S_{BET} (Tab. 1). This couldn't be explained by the traditional viewpoint that the higher S_{BET} the better catalyst activity when taking the activity carbon as the support.[14] It could be seen that the V_p and D_p values of sample D were higher than the others. However, the corresponding values of sample A were higher than those of sample C, the former catalyst activity was lower than the latter. Additionally, the sample B and C had almost the similar textural parameters, however, they had significantly different catalyst activity. All of the above demonstrated that the textural parameters of the support were not the main reason for the different catalyst activity. It was the surface chemical properties that played an important role in the catalyst system, furthermore, it need to be detail studied.

Fig. 1c and Fig. 1d showed the influence of Au^{3+}/Cu^{2+} contents on the structured catalysts supported D on acetylene conversion and C_2H_3Cl selectivity. The amount of Au were each loaded 0.1 wt%, 0.4 wt%, 0.1 wt%, 0.2 wt%, 0,1 wt% and 0 wt% on six corresponding D which were coated by 1.0wt%, 2.5 wt%, 2.0 wt%, 2.5 wt%, 3.0 wt% and 0 wt% Cu, respectively. As can be seen from the results, the catalytic activity improved significantly, when added and improved Au components in the catalysts, as compared with single-component Cu catalysts, which confirmed that $AuCl_3$ played an important role on the catalytic performance. Nevertheless, we found that when both the Au and Cu were added in a certain ratios as shown, the catalyst could keep more satisfactory conversion and lower Au dosage compared with single-component Au catalysts. This result demonstrated that adding $CuCl_2$ compound could reduce the amount of precious metal gold significantly, thus reducing the cost of the catalyst.



(a)



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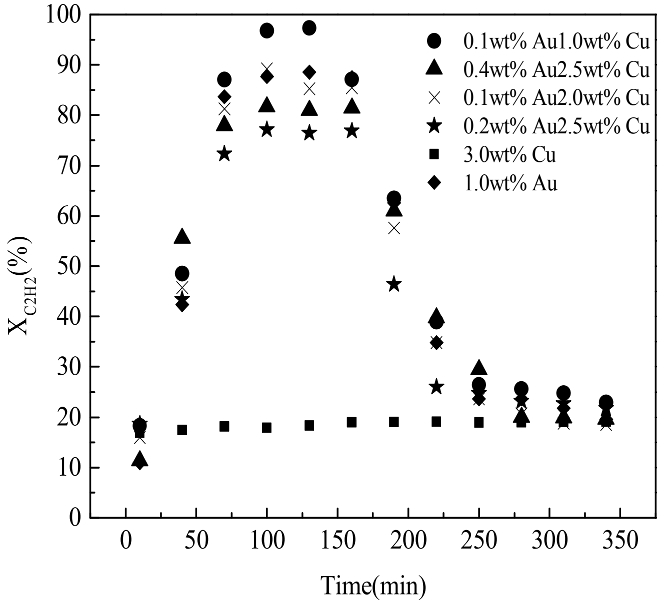

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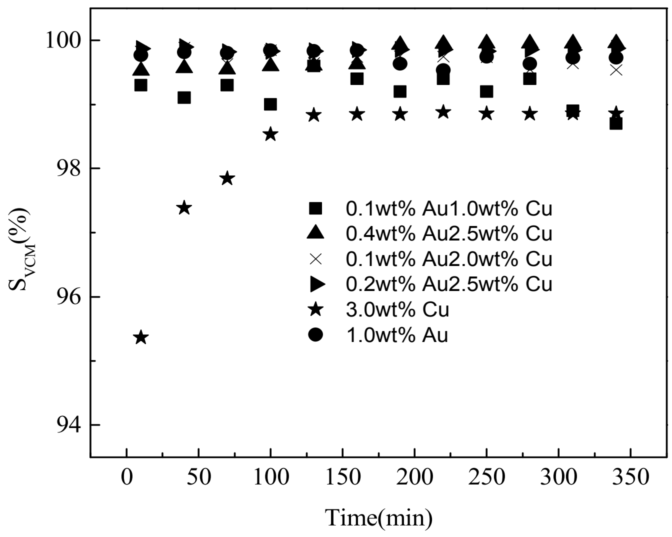


(d)

Fig. 1 Variation curve of (a) C_2H_3Cl selectivity with time (b) C_2H_2 conversion with time. (c)Influence of Au^{3+}/Cu^{2+} contents on the catalysts on acetylene conversion. (d)Influence of Au^{3+}/Cu^{2+} contents on the catalysts on C_2H_3Cl selectivity.

Temperature=150 ℃, Pressure=0.1 MPa, V(HCl):V(C_2H_2)=1.1:1, GHSV=120 h^{-1}

3.2 Characterization techniques

3.2.1 XRD characterization and N_2 adsorption/desorption studies The X-Ray diffraction patterns of the four γ-Al_2O_3 were shown in Fig. S1. They indicated that all the supports had similar crystal structure. The nitrogen adsorption desorption isotherms and the pore size distribution of four γ-Al_2O_3 supports were illustrated in Fig. S2a and Fig. S2b.The textural parameters of the γ-Al_2O_3 were listed in Tab.1. SBET values were obtained within the range of 188.8-310.4 m^2/g. Sample B and C had the similar textural parameters, whose S_{BET} values (295.0 m^2/g and 310.4 m^2/g) were higher than those of sample A and D (244.1 m^2/g and 188.8 m^2/g).

Since the activated carbon surface is very dense, the lack of mesoporous structure[12], lead the $HAuCl_4$ solution cannot enter the inner part of the dense activated carbon pellets. The high density $AuCl_3$ and $CuCl_2$ crystals accumulated on the surface and also in the outer shell of the activated carbon pellets will inevitably aggregate to form large clusters. By contrast, Al_2O_3 is ratherporous[11], leading to good dispersion of the $AuCl_3$ particles, which enhanced the utilization of Au to a certain extent. This result combined with the above-mentioned acetylene conversion can be efficiently proved to Al_2O_3 as supports for preparing catalysts can reduce the Au content.

Table 1 Textural characterization

Sample	S_{BET}(m^2/g)[a]	V_p(cm^3/g)[b]	D_p(nm)[c]
A	244.1	0.495	7.60
B	295.0	0.400	6.25
C	310.4	0.406	6.55
D	188.8	0.486	9.34
Fresh ACAlA	245.3	0.496	7.58
Fresh ACAlB	294.1	0.405	6.26

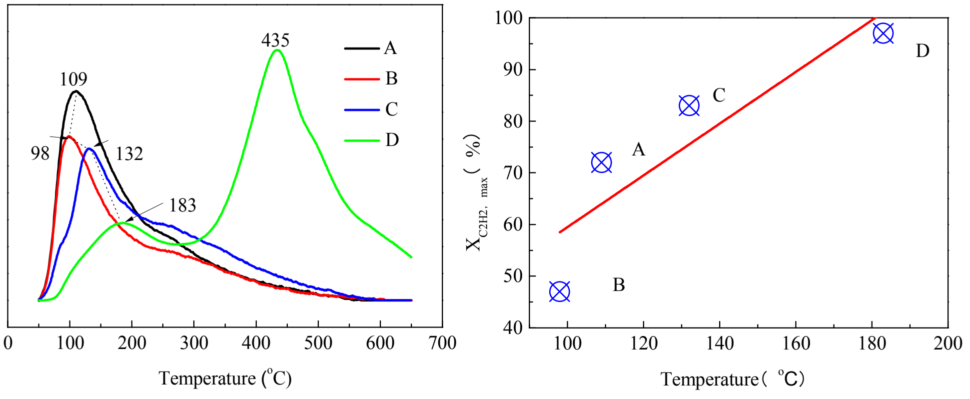
Fresh ACAlC	311.2	0.406	6.53
Fresh ACAlD	186.4	0.493	9.29
Deactivated ACAlD	179.4	0.479	8.89

[a]BET specific surface area; [b]BJH volume of pores; [c]Average pore diameter

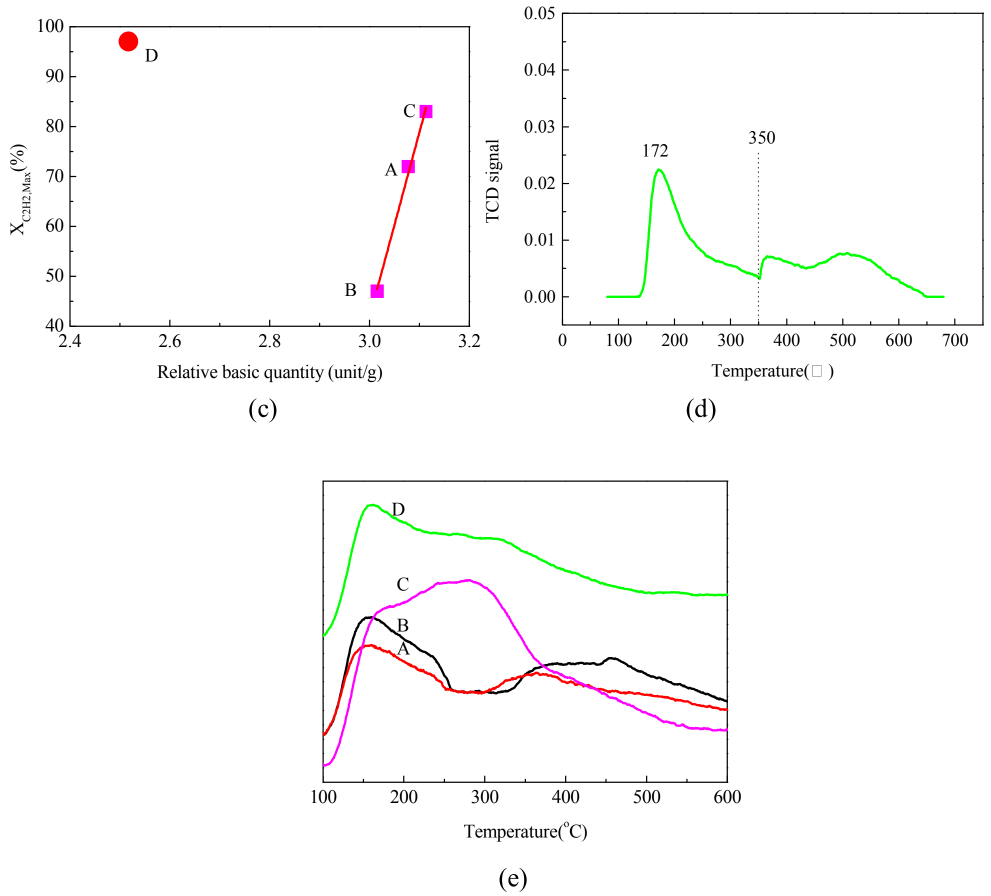
3.2.2 Temperature-programmed analyses The CO_2-TPD profiles for all the pure γ-Al_2O_3 are shown in Fig. 2a. Compared with the sample A, B and C, a middle desorption peak and a strong desorption peak could be observed in the profile of sample D, which indicated that the sample D had a middle and a strong base site. In addition, there was a considerable difference in the weak base site among the four samples. The shifts in desorption peaks of weak base site were related to $X_{C2H2,\ max}$, it could be observed that the two values revealed positively proportional relationship (Fig. 2b), namely the higher shift temperature, the higher $X_{C2H2,\ max}$. That is to say strengthening the weak base site of the γ-Al_2O_3 support could enhance the activity of the catalyst of $AuCl_3$-$CuCl_2$/γ-Al_2O_3, the amount of the base sites (including the middle and strong base site in sample D) of the four samples was also related to the $X_{C2H2,max}$, the profile performed liner relation (Fig. 2c). Curiously, sample D had the least amount of base sites, but it had the highest catalyst activity. This could be explained for the excess middle and strong base site in sample D. To ensure the above conclusion, a CO_2-TPD experiment was conducted to the fresh ACAlD catalyst and it was shown in Fig. 2d. It can be clearly seen that the strong base site of above 350 ℃ on the alumina D is reduced. It may be the reason that there is an interaction effect between Au^{3+} and the strong base site on the alumina surface when absorbed.

On the other hand, the NH_3-TPD patterns are shown in Fig. 2e. All the samples had a weak acid site and sample A, B, D had the similar weak acid with desorption peak of about 150 ℃, while the tail of the desorption peaks of sample D was shifted to higher temperatures (about 450℃). In addition, according to the size of the area under the NH_3-TPD profiles, with the following order of the amount of acid sites: D > C > A > B. Among them, sample C had an obvious feature of middle acid sites, and a handful of strong acid sites in sample A and D could be observed. Although some efforts had been made to correlate the C_2H_2 conversion with the acid strength and amount of the acid sites, just as the above method of investigation on the base site, it showed that no clear trend was observed between the acid properties of the support and the overall rate of C_2H_2 conversion.

It has been investigated that the influence of the base site of the catalysts activity taking different γ-Al_2O_3 as the support. The H_2-TPR profiles of the fresh ACAlA, ACAlB, ACAlC, ACAlD were shown in Fig. S3 and the TEM images of them were shown in Fig. S4. They indicated that the base site on the surface of the γ-Al_2O_3 support had a positive effect to the dispersion of the activity ingredient.



(a) (b)



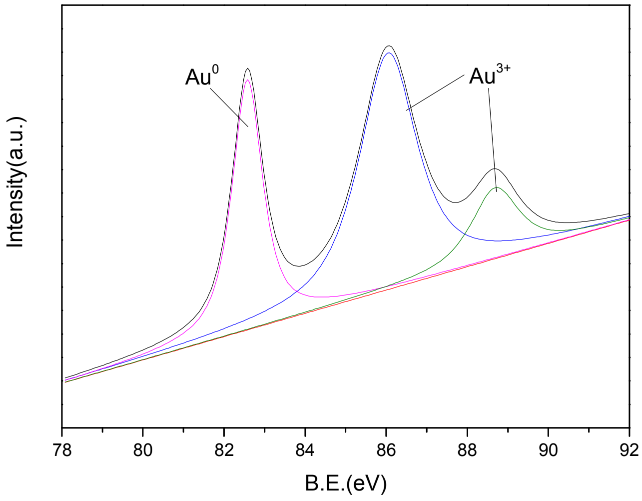
(c) (d)

(e)

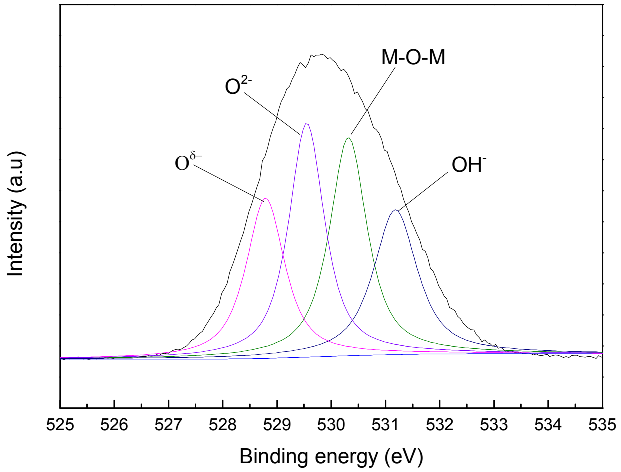
Fig. 2 TPD profiles and correlation (a) CO_2-TPD profiles of alumina A, B,C and D;(b) Correlation between catalytic activity and basic strength ; (c) Correlation between catalytic activity and relative basic quantity; (d)CO_2-TPD profile of fresh ACAlD;(e) NH_3-TPD profiles of alumina A, B,C and D.

3.2.3 X-ray Photoelectron Spectroscopy (XPS) To further demonstrate basic sites and determine the oxidation states of the surface Au sites on the catalysts[17] surface, the XPS spectra of the fresh ACAlD catalyst corresponding to Au 4f peaks and O1s peak were shown in Fig. 3. Three broad peaks appeared over the Au 4f region which could be deconvoluted to components due to $Au(OH)_3$, Au_2O_3, and metallic Au. The Au^0 $4f_{7/2}$ peaks were detected at a range of binding energy of 83.0-83.1 eV, which was typical of metallic gold, and the spectra with binding energies at 86.2 and 89.9 eV were attributed to the presence of Au in the form of Au^{3+}

[18]. From the binding energy of the O1s XPS, we could determine different basic sites on the catalyst surface. All of the O (1s) signals, wide and asymmetrical, have been deconvoluted into four components responding to diversified O atoms species, which noticed the presence of oxygen atoms in four different chemical environments, including OH^- peaks at about 531-532 eV, lattice oxygen complex metal oxides, such as M-O-M, at 530.1 eV, O^{2-} in CuO at 529.6 eV and a relatively strong peak at lower binding energy about 528.5 eV, which could be attributed to the low-coordinated $O^{\delta-}$.[19] Based on these two points aboved, it could be concluded that catalyst surface contained different chemical groups and by anchoring these chemical groups, active site could more effective loaded on the catalyst surface.



(a)



(b)

Fig. 3(a) XPS spectra of Au 4f in fresh ACAlD catalyst (b) XPS spectra of O1s spectrum in the fresh ACAlD catalyst.

3.3 The support modification initially by potassium hydroxide

Cornelius [20] reported that it produced O^{2-} or O^{-}, which can provide the Lewis base site on the surface of Al_2O_3 during the process of dehydration after calcination. It may be the different oxygen centers of the O^{2-} or O^{-} on the surface of Al_2O_3 could affect the nucleation process of Au^{3+} and Cu^{2+} species adsorbed on the surface. And this could lead to different particle size of activity ingredient on per different supports (Fig. S5), however the mechanism should be further studied.

To confirm the surface base site of the support play an important role in the excellent performance of alumina, the alumina B, which had the worst catalytic performance, was modified initially by potassium hydroxide. After being cleaned by hydrochloric acid, the alumina B was impregnated for 10 hrs by 5 mol/l potassium hydroxide solution and then it was dried. The obtained sample was denoted as MB. As the above mentioned steps were done, the catalyst named MACAlB was also prepared and took MB as the support. The CO_2-TPD profile of MB was shown in Fig. S6, we could see that an obvious strong base site appeared. Compared with ACAlB, the catalytic performance (Fig. 4) of MACAlB had improved significantly and the highest conversion rate was increased from 51% to 82%. To account for the surface groups of the supports, the IR spectra of different samples(C, B, MB, ACAlB, MACAlB) were analyzed. As can be seen from Fig. 5, the obvious bands were observed at 3497.08 cm^{-1} and 1640 cm^{-1}, which were hydroxyl absorption peak of water. 729.45 cm^{-1}, 566.09 cm^{-1} were regarded weak absorption peak of γ-Al_2O_3. There were two obvious differences in the patterning between the fresh and modified catalysts: characteristic peaks of hydroxyl radical from Al–OH on the surface of γ-Al_2O_3 at 1161 cm^{-1} and 1437 cm^{-1} peak was characteristic absorption peaks of AlO_2^-.[21] We found that when loaded active metal, peaks of AlO_2^- became weaker, which indicated the process of loading caused the electron transformation. Accordingly, a strong effect of the surface chemistry of modified Al_2O_3 on the Au-Cu/Al_2O_3 catalytic activity contacted with Fig. 4 was observed.

In addition, the life span had also extended. It ensured that the base site of the support had played an important role in improving the catalyst activity and its life span.

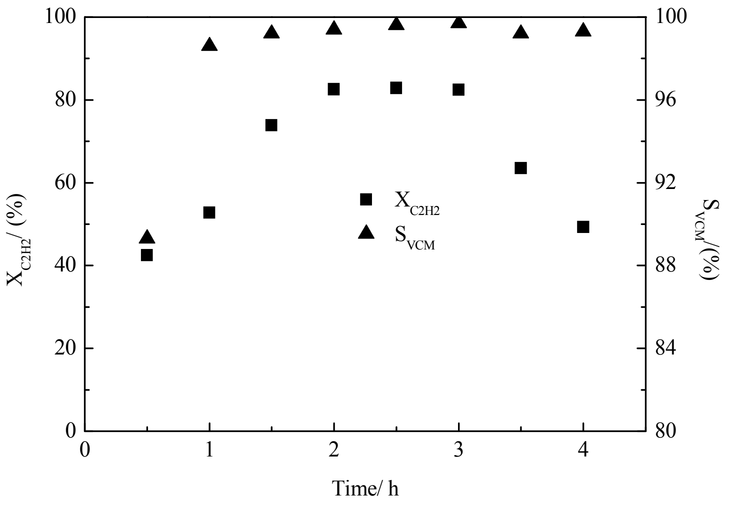


Fig. 4 Variation curve of C_2H_2 conversion and C_2H_3Cl selectivity with time of MACAlB.

Temperature=150℃, Pressure=0.1 MPa, V(HCl):V(C_2H_2)=1.1 : 1, GHSV=120 h^{-1}

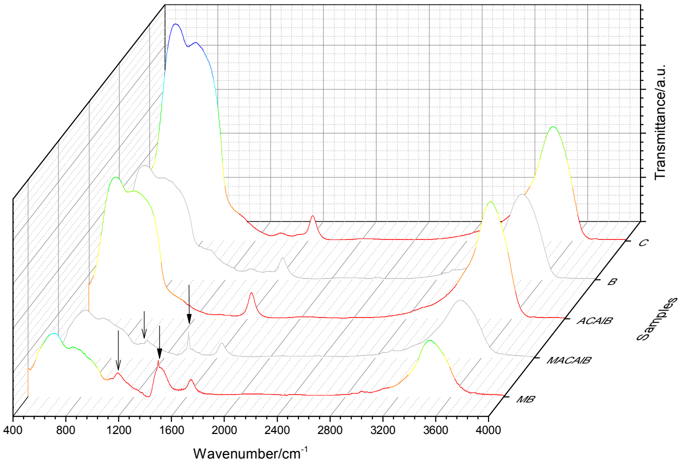
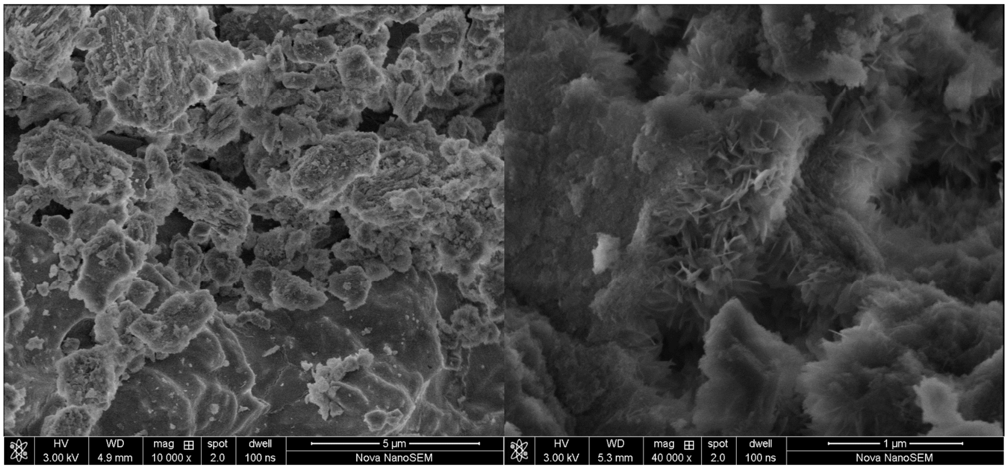


Fig. 5 IR spectra of pure support C, support B, the fresh catalyst ACAlB, the modified catalyst MACAlB and the modified support MB.

3.4 Deactivation analysis

The specific surface area and pore structure parameters of both fresh ACAlD and deactivated ACAlD catalyst were shown in Tab. 1. It can be seen that the parameters of the fresh catalyst were similar to the support, which suggested that it did not produce the reunion and bridging phenomenon with small particle size of $AuCl_3$ and $CuCl_2$ loaded on the mesoporous pore surface of γ-Al_2O_3. There was nearly no change of channel and specific surface area of the fresh catalyst with the support. However, the parameters of the deactivated catalyst were reduced. It seemed that there was a phenomenon of channel jam in the catalyst during the reaction.

The SEM images of fresh and deactivated catalyst were shown in Fig. 6. It can be seen clearly that the channel of the fresh catalyst (Fig. 6a) was relatively abundant. However, it was covered with a layer of carbon deposition which was "chip" structure on the surface of deactivated catalyst (Fig. 6b).The "chip" structure deposition covered on the activity site and was produced quickly and easily, it was one reason for the catalyst's short life span. In addition, it was consistent with the result of N_2 adsorption and desorption analysis (Tab. 1).



（a） （b）

Fig. 6 SEM images of (a) fresh catalyst; (b) deactivated catalyst.

In order to provide direct evidence of coke deposition, TGA experiments were performed under air atmosphere and the results were shown in Fig. 7. The amount of coke deposition should be equal to the difference in weight loss between the fresh and deactivited catalysts within the temperature range of coke burning. The mass losses of fresh and deactivated ACAlD catalysts in the range of 100–500 ℃ was 3.9% and 21.9%, respectively, which indicated that the actual amount of coke deposition was 18.0 %. It also demonstrated that the coke deposition could be nearly burned off under the temperature of 500 ℃in air atmosphere.

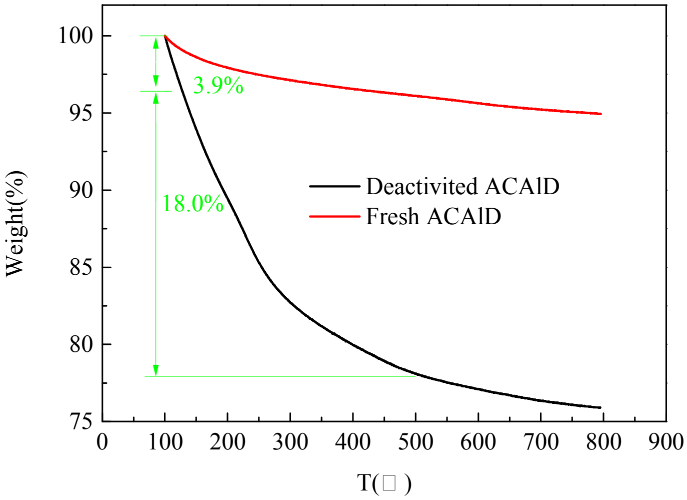


Fig. 7 TGA profiles of fresh ACAlD and deactivated ACAlD.

3.5 Regeneration studies

Due to the high price of noble Au, the possibility of reusing the catalyst was also investigated (Fig. 8). The deactivated catalyst can be easily regenerated by roasting at 500 ℃ in air atmosphere for 10 min. The process was simple and the high mechanical strength of the γ-Al_2O_3 support guaranteed the intact shape of the catalyst when loading and unloading. It can be seen that the acetylene conversion rate can reach 96% and vinyl chloride selectivity was more than 99% for the first regenerated catalyst, which was nearly the same catalytic performance as the fresh catalyst. Although the activity of second regeneration catalyst with the acetylene conversion rate of 92% was reduced. It also showed an easy and efficient regeneration performance.

Besides, it is generally believed that the Au^{3+} is the active component of the catalysts for acetylene hydrochlorination reaction. The activity recovery of regenerated catalyst also showed that the reduction and the running off of Au^{3+} were not the main reasons for the catalyst deactivation.

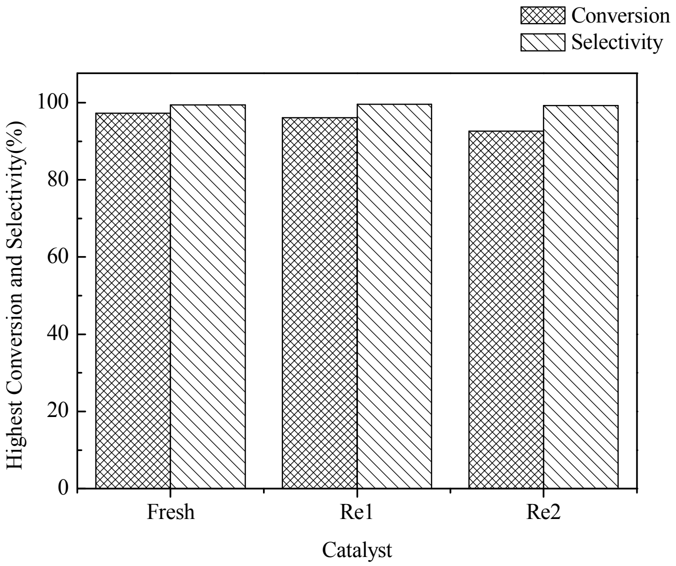


Fig. 8 The highest C_2H_2 conversion and C_2H_3Cl selectivity of the fresh and regeneration catalyst.

Temperature=150 ℃, Pressure=0.1 MPa, $V(HCl):V(C_2H_2)=1.1 : 1$, GHSV=120 h^{-1}

4. Conclusions

γ-Al_2O_3 was less used as an efficient support to prepare catalyst for acetylene hydrochlorination compared with other carriers. The $AuCl_3$-$CuCl_2$/γ-Al_2O_3 catalyst can attain 97% conversion rate in acetylene conversion which was close to that in taking the activity carbon as the support. The results showed that γ-Al_2O_3, known as a support had better mechanical strength and mesoporous (20~50 nm) structure, was one of potential supports for $AuCl_3$-$CuCl_2$ bimetal catalyst. It was the strong base site instead of the texture properties or the acid site that determined its unusual activity with others. Furthermore, by modifying the support with potassium hydroxide can increase the activity and prolong the life span. The carbon deposition was the main reason for its fast deactivation and the actual amount of coke deposition was 18.0%. Although with short life-span at present, its thermostability and mechanical strength revealed the excellent regeneration ability. Therefore it is believed that γ-Al_2O_3 has a great potential to be applied in view of its increased life span and reduced cost. In the meantime this should be further studied in the future work.

Acknowledgments

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Reference

[1] X. B. Wei, H. B. Shi, W. Z. Qian, G. H. Luo, Y. Jin, F. Wei, *Ind. Eng. Chem Res.*, 2009, **48**, 128.

[2] G.J. Hutchings, D.T. Grady, *Appl. Catal.*, 1985, **17**, 155.

[3] N. Pirrone, S. Cinnirella, X. Feng, R. Finkelman, H. R. Friedli, J. Leaner, R. Mason, A. B. Mukherjee, G. B. Stracher, D. G. Streets, K. Telmer, *Atmos. Chem. Phys.*, 2010, **10**, 5951.

[4] H. Z Gu, X. S. Xu, A. A. Chen, A. Ping, X. H. Yan, *Catal. Commun.*, 2013, **41**, 65-69.

[5] B. B. Chen, X. B. Zhu, M. Crocker, Y. Wang, C. Shi, *Catal. Commun.*, 2013, **42**, 93.

[6] M. Conte, A. F. Carley, C. Heirene, D. J. Willock, P. Johnston, A. A. Herzing, Kiely CJ, Hutchings GJ, *J Catal.*, 2007, **250**, 231.

[7] M. Conte, A. F. Carley, G. Attard, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.*, 2008, **257**, 190.

[8] S. J. Wang, B. X. Shen, Q, L Song, *Catal. Lett.*, 2010, **134**, 102.

[9] X. B. Wei, F. Wei, W. Z. Qian, G. H. Luo, H. B. Shi, Y. Jin, *J. Process Eng.(Chinese)*, 2008, **8**, 1218.

[10] H. Y. Zhang, B. Dai, X. G. Wang, L. L. Xu, M. Y. Zhu, *J. Ind. Eng. Chem.*, 2012, **18**, 49.

[11] J. Zhao, X. Cheng, L. Wang, et al, *J Catal*, 2014, DOI 10.1007 / s10562-014-1371-9.

[12] X. Yang, C. Jiang, Z. Yang, *J. Mater. Sci. Technol*, 2014, **30**, 434-440.

[13] X. G. Cheng, J. G. Zhao, L. Wang, R. F. Ren, H. H. Yang, B. X. Shen, *Chem. J. Chin. Univ.(Chinese)*, 2014, **3**, 582.

[14] H. L. Chih, D. L. Shawn, JyhFL, *Catal. Lett.*, 2003, **89**, 235.

[15] J. C. Yeong, T. Y. Chuin, *J. Catal.*, 2001, **200**, 59.

[16] L. J. Marta, J. Wojciech, B. Magdalena, K. Zbigniew, K. Leszek, K. Zbigniew, *Top. Catal.*, 2009, **52**, 1037.

[17] E. D. Park, J. S. Lee, *J. Catal.*, 1999, **186**, 1-11.

[18] J. Zhao, J. Xu, Xu J, *J. Chem. Eng.*, 2014, **262**, 1152–1160.

[19] J. Okal, W. Tylus, L. Kępiński, *J. Catal.*, 2004, **225**, 498-509.

[20] E. B. Cornelius, T. H. Milliken, G. A. Mills, A. G. Oblad, *J. Phys. Chem.*, 1955, **59**, 809.

[21] S. L. Wang, C. T. Johnston, D. L. Bish, *J. Colloid. Interface. Sci.*, 2003, **260**, 26-35.

[22] J. Ma, S. Wang, B. Shen, *J. EACT KINET MECH CAT.*, 2013, **110**, 177-186.