Preparation of Au/C catalysts using microwave-assisted and ultrasonic-assisted methods for acetylene hydrochlorination

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ABSTRACT

In the present work, the catalytic performance of Au/C catalysts prepared by ultrasonic-assisted, microwave-assisted and incipient wetness impregnation techniques for the hydrochlorination of acetylene to vinyl chloride monomer (VCM) was studied. The catalyst prepared by the ultrasonic-assisted technique significantly exhibited enhanced acetylene conversion activity and selectivity to VCM over a period of 20 h of evaluation. The effect of gold loading on catalyst performance was determined, from which 1% Au was found to be the optimum loading compared to 0.5% and 2.0% loading. Importantly, the effect of different catalyst pretreatments (i.e. with and without H_2/HCl and HCl purging prior to the reaction testing) on the catalytic performance was also identified. The use of different pretreatment procedures affects only the initial activity of catalyst, while the long-term activities of catalyst with different pretreatments are almost identical.

1. Introduction

Polyvinyl chloride (PVC) is the third highest global volume plastic after polyethylene and polypropylene, and the demand increases annually. In 2008, the PVC world market reached a volume of 34 million tons, whereas in the year 2000 demand amounted to 24 million tons. Moreover, the PVC demand is expected to be total more than 40 million tons in the year 2016 [1]. PVC is produced from polymerization of vinyl chloride monomer (VCM), which is typically produced industrially by the dehydrochlorination of dichloroethane (ethylene-based process) or hydrochlorination of acetylene (acetylene-based process). In China, the world's largest producer of PVC, the PVC capacity has increased more than 20% annually since 2000 and became greater than that of the United States in 2005. Currently, PVC production through the acetylene-based process accounts for about 70% of the total PVC production capacity in China [2].

In the commercial acetylene-based process, acetylene (C_2H_2) gas reacts with anhydrous hydrogen chloride (HCl) gas over carbon-supported mercuric chloride to produce vinyl chloride monomer (VCM). This reaction is exothermic and highly selective at an optimum reaction temperature of about 170–180 °C [3–5]. The major problem of this process is sublimation of mercury, arising from reduction of mercuric chloride during the reaction. This not only affects catalyst deactivation but also causes severe safety and environmental problems [6]; alternative catalysts are thus needed. Previous workers have reported a direct correlation between the standard reduction potential of noble metals and acetylene conversion and concluded that gold is a potential catalyst to replace the mercuric chloride as the preferred catalyst for this reaction [4–9]. However, the lifetime of gold catalysts is relatively short and the rate of deactivation is dependent on temperature. At higher temperatures (>100 °C), deactivation is due to reduction of Au^{3+} to Au^0 while carbon deposition causes catalyst deactivation at lower temperatures (<100 °C). However, even though catalyst deactivation was minimized at 100 °C, catalytic activity was too low at this temperature [8]. Several groups have shown that carbon-supported gold catalysts offer high initial activity; however, reduction of Au^{3+} (presumed to be the active site) to Au^0 and subsequent sintering as well as poor distribution of Au particles on the carbon support result in rapid loss of activity [9].

Recently, there have been several attempts to synthesize supported metal catalysts with high dispersions using microwave-assisted or ultrasonic wave-assisted techniques. It is known that an important parameter for catalyst synthesis by drying with

microwave irradiation is proper contact time. For normal drying processes, the solvent is heated by conduction and convection, which typically results in large temperature gradients within the solvent and catalyst support [10]. For the ultrasonic-assisted technique, the ultrasound wave enhances good mass transport and even thermal distribution throughout the impregnation solution and the pores of the catalyst support using the cavitation phenomenon typical of ultrasonic methods. Other desirable physical phenomena include formation, growth and collapse of bubbles in the liquid medium. In contrast, the microwave-assisted technique can assist catalyst synthesis by modifying the shape of the supported metal to be quasi-spherical in morphology. Moreover, the catalyst preparation time can be reduced by this technique [11–13]. For the ultrasonic-assisted technique, the ultrasound wave improves mass transport, emulsification, thermal heating, and a variety of support effects by the phenomenon of cavitation which involves formation, growth and collapse of bubbles in the liquid medium. Consequently, catalyst particle diameters may be decreased, surface defects can be introduced on the particle surface, and the surface area of the support may be increased [14,15]. In the present work, Au/C catalysts having high Au dispersion have been synthesized by microwave-assisted and ultrasonic wave-assisted techniques, and their catalytic activities for acetylene hydrochlorination have been studied and compared to catalysts prepared by typical incipient wetness methods. Finally, the effects of gold weight loading and pretreatment options on the catalyst performance were also investigated.

2. Experimental

2.1. Catalyst preparation

A conventional Au/C catalyst was first prepared by incipient wetness impregnation using concentrated aqua regia as a solvent [16]. The carbon support (coconut shell-based and supplied by Carbokarn) was initially washed with dilute, aqueous HCl (1 M) (Qrec HCl 37%) to eliminate impurities. The carbon was washed thoroughly by distilled water and then filtered and dried overnight at 110 °C. A solution of $HAuCl_4 \cdot xH_2O$ (Sigma–Aldrich: 50% gold assay) in concentrated >aqua regia solvent (mixture of HCl (Qrec HCl 37%): HNO_3 (Qrec HNO_3 67%) = 3:1) was added drop-wise to the activated carbon while stirring about half an hour. Then the impregnated catalyst was then dried overnight at 110 °C in the oven (CI sample). Alternatively, the ultrasonic-assisted (UL sample) preparation was prepared by ultrasonically-agitating the dissolved $HAuCl_4$ in aqua regia solution and carbon support in an ultrasonic bath (Crest Ultrasonic Model: 275HTAE 42–45 kHz) and maintaining at 45–50 °C for 6 h [17]. The microwave-assisted technique (MW sample) was applied during the drying stage of the impregnated carbon support microwave-assisted preparation by using a microwave oven (Sanyo EMS 1063s 800W compact microwave) for 2 min.

2.2. Catalyst characterization

X-ray diffraction (XRD) was used to investigate the crystalline characteristics of the catalysts. The XRD spectra of catalysts were measured by a Rigaku MiniflexII with a Texultra detector using Cu K_α radiation over the 2θ range from 20° to 80°. The analysis of elemental compositions and oxidation states of catalyst surfaces was determined by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra DLD instrument equipped with a monochromated Al K_α X-ray source and hemispherical analyzer capable of an energy resolution of 0.5 eV. Temperature-programmed reduction (TPR) was used for determining the reduction temperature of Au^{3+}, using a Micromeritics Chemisorb 2920, with 10% H_2 in Ar (50

SCCM total flow) and a temperature ramp rate of 5 °C/min from 25 °C to 500 °C. Gold weight loadings were determined by atomic absorption (AAnalyst 400; PerkinElmer) after digestion of the Au/C catalyst in aqua regia at 110 °C for 4 h and then filtering of the solid catalyst from the solution containing the Au salt. Finally, the BET surface areas of the supported Au catalysts were determined using a Micromeritrics ASAP 2020. The measurements were performed by degassing of the sample at 120 °C for 12 h prior to using N_2 as the adsorbate at −196 °C. The specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) method while the pore volume, average pore diameter, and pore size distribution were calculated using Barrett–Joyner–Halenda (BJH) desorption branch analysis and t-plot micropore area analysis.

2.3. Catalyst evaluation

Acetylene hydrochlorination using the supported Au catalysts was carried out in a fixed bed reactor (Pyrex glass tube, 3/8″ OD). The C_2H_2 feed gas was treated to remove acetone inhibitor by passing through a molecular sieve 5A trap and then added along with He diluent to a flow of anhydrous HCl (Praxair, 99.999% HCl purity) before feeding to the reactor. The following reaction protocol was used for all catalysts. The reactor loaded with fresh catalyst was dried in flowing helium at 120 °C for 30 min to remove residual H_2O and then pre-chlorinated using a flow of He and HCl (1: 1 ratio) at 180 °C for 1 h. Acetylene was then added at a desired flow to give a feed composition of C_2H_2: HCl: He = 1.0: 1.1: 1.0 at an initial reaction temperature of 180 °C. The exit gas from the reactor was passed through a temperature-regulated scrubber (15 °C) containing 5 M NaOH solution to absorb unreacted HCl. The gaseous products were analyzed by an on-line gas chromatograph (model HP5890 with FID detector using a capillary column of Agilent J&W HP-Plot Poraplot Q column). Acetylene conversion and VCM selectivity were calculated by mass balance methods. The fractional conversion of C_2H_2 was determined using the standard formalism of $(C_2H_{2(in)} − C_2H_{2(out)})/C_2H_{2(in)}$ and VCM selectivity was calculated from the amount of VCM formed/amount of total products formed. Since only C_2 products were observed, no normalization to VCM was required.

3. Results and discussion

3.1. Effect of catalyst preparation technique

The comparative X-ray diffraction (XRD) patterns of freshly-prepared (no pretreatments) conventional (CI), ultrasonic-assisted (UL), and microwave-assisted (MW) catalysts are shown in Fig. 1. None of the catalysts shows peaks indicative of any Au^0 or gold salt species, indicating that all Au species are present in either amorphous or very small, highly dispersed particles. Thus, Au^0 particle sizes must be <4 nm or most of the Au exists as non-crystalline Au^{3+} species [18]. For Au^0/C catalysts, the typical peaks of Au^0 at 2θ = 38.2, 44.4, 64.7 and 77.7°, assigned to the diffraction lines of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) facets of gold, respectively, are expected [19].

The methods of catalyst preparation also affect the physical properties of the carbon support. Support analyses data are summarized in Table 1. Impregnation of the Au salts lowers the surface area of the support, as expected. The effect is most pronounced for the CI sample. Both MW and UL effects decrease the loss of surface and also maintain the more desirable larger pore diameters of the carbon micropores. This phenomenon of the UL sample is likely due to the tiny bubbles formed by the vibrations which collapse and then re-form from the cavitation phenomena. This occurs when the expansion speed of bubbles is high enough and the inertial power is
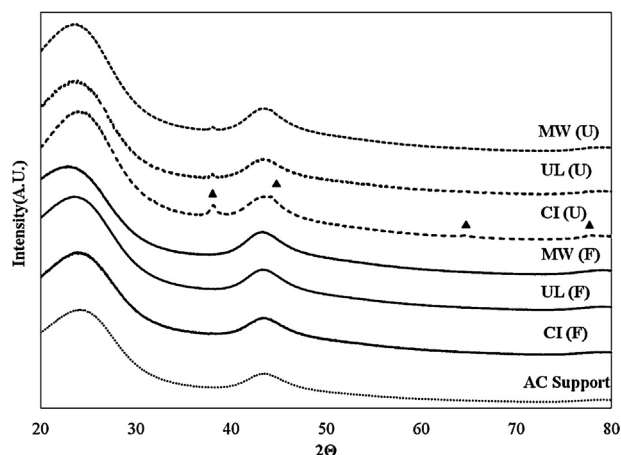
Fig. 1. XRD spectra of catalysts from different preparation methods; conventional impregnation (CI), ultrasonic-assisted (UL), and microwave-assisted (MW). "F" denotes fresh catalyst before reaction and "U" denotes used catalyst, after reaction. The black triangles mark the 2θ values where Au^0 diffraction peaks would be expected. The 2θ values = 38.2, 44.4, 64.7 and 77.7 correspond to the diffraction lines of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) facets of gold metal.
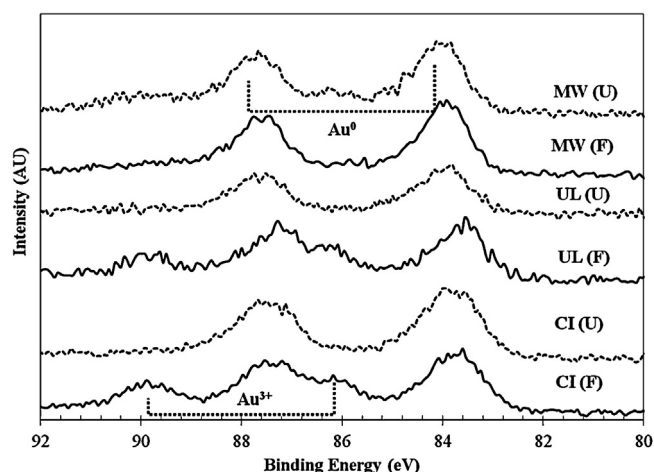

Fig. 2. Gold 4f 7/2 and 4f 5/2 binding energies XPS spectra of catalysts prepared by different methods; conventional method (CI), ultrasonic-assisted (UL) and microwave-assisted (MW). Fresh and used catalysts denoted as F and U, respectively. Binding energy values have been referenced to C1s peak at 284.6 eV. Literature values for Au 4f 7/2 binding energies of Au^0, Au^+, and Au^{3+} are 83.9, 85.0, and 85.7 eV, respectively [20].
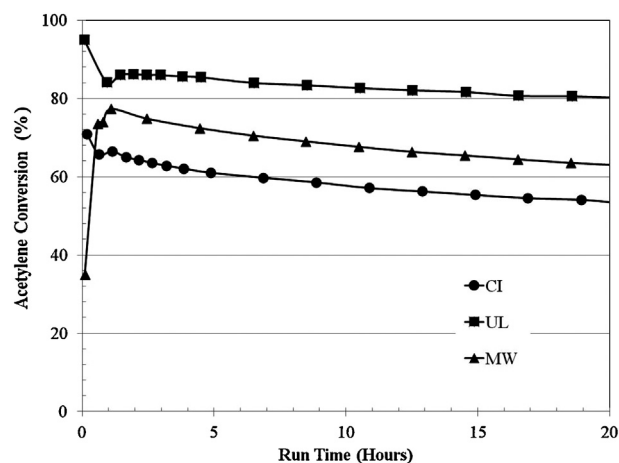
also very high, so that the bubbles cannot contract and thus remain in an expanding mode. Bubble collapse can also cause a micro high speed flow within the pores, causing unwanted local hotspots [15].

In previous work [5–9], the active Au species for acetylene hydrochlorination has been inferred to be in the Au^{3+} oxidation state. Thus, XPS analysis was carried out to determine and quantify the oxidation states of the surface Au sites on the different catalysts. Both fresh catalysts (no pretreatment) and catalysts after reaction (used) were analyzed. All Au peaks were referenced to the C1s binding energy (BE) of the support at 284.6 eV. As shown in Fig. 2 and Table 2, the CI and UL samples contain a higher fraction of Au^{3+} than the MW sample. The reference values for Au 4f 7/2 binding energies of Au^0, Au^+, and Au^{3+} are listed in Fig. 2 [20]. The XPS peak positions for the fresh catalysts are similar, but the normalized intensities for each catalyst depend on the contribution of the Au^{3+} peak. The XPS spectra for all used catalysts, however, show that the surfaces have been reduced to Au^0; the presence of Au^{3+} is not obvious.

The catalyst evaluation data in Fig. 3 shows that CI and UL samples have higher initial activities than the MW sample and that after 20 h operation the UL sample exhibits significantly higher acetylene conversion than either the CI or MW sample. In all cases, selectivity to VCM was more than 99.5% VCM with 1,2 dichloroethane (EDC)

Fig. 3. Evaluation of catalysts prepared by different methods (T = 180 °C, P = 1 atm, HCl: C$_2$H$_2$: He feed composition = 1.1: 1: 1 and GHSV = 1480 h^{-1}).

Table 1
BET surface areas and pore analyses of the carbon support (CK) and fresh catalysts prepared by conventional impregnation (CI), ultrasonic-assisted (UL), and microwave-assisted (MW) methods.

Sample	Au loading[a] %	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
CI	1.04	687	0.33	1.98
MW	0.98	883	0.58	2.66
UL	1.08	861	0.59	2.76
Support (CK)	–	940	0.48	2.57

[a] Values measured by AA after dissolution of Au using concentrated aqua regia.

Table 2
Identification of Au species from XPS for different Au/C catalysts (the Au^0 and Au^{3+} 4f 7/2 peak intensities are normalized to C1s intensity at 284.6 eV).

Preparation method and catalyst status		Au^{3+} (eV)	Au^0 (eV)	Au^{3+} (%[a])	Au^0 (%)
CI	Fresh	86.21	83.76	38	62
	Used	–	83.87	–	100
UL	Fresh	86.14	83.65	36	64
	Used	–	83.99	–	100
MW	Fresh	–	83.93	–	100
	Used	–	84.13	–	100

[a] The % is percentage ratio of integrated area Au^x and total Au area of Au^{3+} and Au^0 that was calculated from XPS peak program.

Fig. 4. Effect of Au loading for UL catalysts on catalytic activity (T = 180 °C, P = 1 atm, HCl: C_2H_2: He feed composition = 1.1: 1: 1 and GHSV = 1480 h^{-1}).

Fig. 5. XPS spectra for 0.5, 1.0, and 2.0 wt% Au/carbon samples prepared by ultrasonic-assisted method (UL). (F: fresh catalyst, U: used catalyst). See Fig. 2 for BE assignments.

as the only trace product. The results in Fig. 3 clearly indicate that "longer term" catalyst activity is not correlated to the amount of Au^{3+} as observed by XPS (Table 2) after reaction. Conte et al. [21] have also investigated the effect of Au^{3+} content on Au/C activity by preparing a set of catalysts with different Au^{3+} content and reported that the most active catalyst was not the catalyst with highest Au^{3+} content. Nevertheless, this study shows the amount of Au^{3+} does affect the initial activity of the catalyst; the fresh MW sample which contains no detectable Au^{3+} also has the lowest initial catalytic activity. Its activity then increased dramatically within 2 h, indicating the formation of a more active surface composition. Since XPS analysis of all used samples showed no presence of Au^{3+}, it is difficult to attribute the higher activity to the formation of Au^{3+} sites. Regardless, the Au/C prepared by the ultrasonic wave-assisted technique showed the highest overall activity and a lower rate of activity loss after 20 h reaction time. Thus, the UL sample was chosen for further studies. It should be noted that for the best of our knowledge, there is still no commercial catalyst prepared by ultrasonic and microwave methods. However, these technologies have been successfully implemented in some industries such as food industry [22,23]. Therefore, it is expected that they can soon be employed for commercial catalyst preparation.

3.2. Effect of gold catalyst loading

The effect of gold loading for UL-prepared catalysts was studied over the range of 0.5 to 2.0 wt%. As shown in Fig. 4, the catalytic activity does not increase with increasing Au amount. The 2.0% Au/C sample shows relatively high acetylene conversion at the first two hours, which could be due to the high Au^{3+} content (according to the XPS analysis in Fig. 5 and Table S1), but its activity has decreased dramatically after 15 h. In contrast, 0.5% Au/C sample shows low initial acetylene conversion but its activity increases steadily and becomes more active than 2.0% Au/C sample after 20 h. The activity of the 0.5 wt% Au sample ends up being considerably lower, however, than the 1.0% Au/C sample. The XRD patterns of the fresh and used catalysts that were evaluated in Fig. 4 are shown in Fig. 6. It can be seen that the fresh catalysts exhibit only the amorphous diffraction peak of the activated carbon support, meaning the Au species were either very small and/or amorphous in structure. However, the 2.0% Au/C catalyst after reaction clearly shows the Au^0 (1 1 1) peak at 38.2°. Similarly, a much smaller Au (1 1 1) peak is observed for the 1 wt% Au sample. Based on Scherrer's equation, the calculated sizes of Au^0 using only the (1 1 1) reflection for 2.0% and 1.0% Au/C are 16 nm and 4.6 nm, respectively. This confirms that the higher weight loadings of Au undergo sintering to larger particles
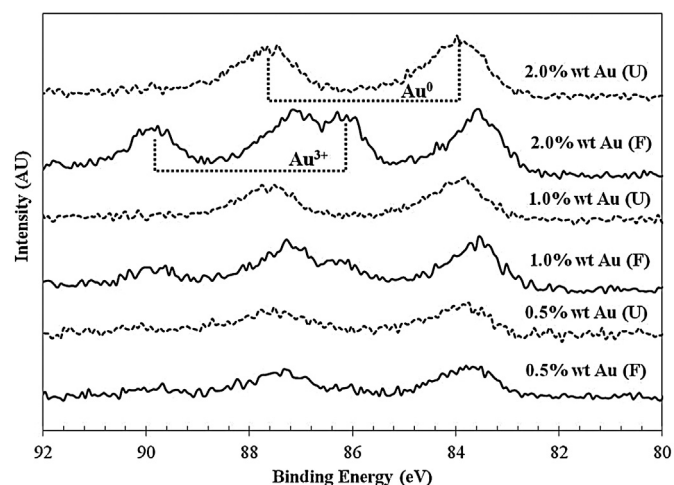
with increasing reaction time. The highest Au particle density on the carbon surface of the 2 wt% Au sample favors thermal sintering relative to the 1.0 and 0.5 wt% Au samples. These sintering tendencies are reflected in the activity data in Fig. 4. A loading of 1.0% Au gives the best balance of resistance to sintering and concentration of active surface sites.

3.3. Effect of catalyst pretreatment

The catalyst performances with different pretreatment procedures are shown in Fig. 7. The pre-chlorinated sample (Task 1) shows the highest initial activity, while the reduced-only sample (Task 4) has the lowest initial activity. Nevertheless, all catalysts exhibit very similar performances behavior after 3 h reaction for the remainder of the evaluation period (20 h). Not only are reaction rates the same, the rates of catalyst deactivation are very similar. Regardless of pretreatment options, the same active Au surface exists after an initial reaction period. Hence, it is misleading to assess catalyst performance for fewer than 5 h of run time as has been done by others [4–9,21,24]. The sample that was pre-chlorinated following reduction at 180 °C (Task 3) has the same initial (and long term performance) as the sample that was only reduced before reaction (Task 4). This shows that on-line HCl
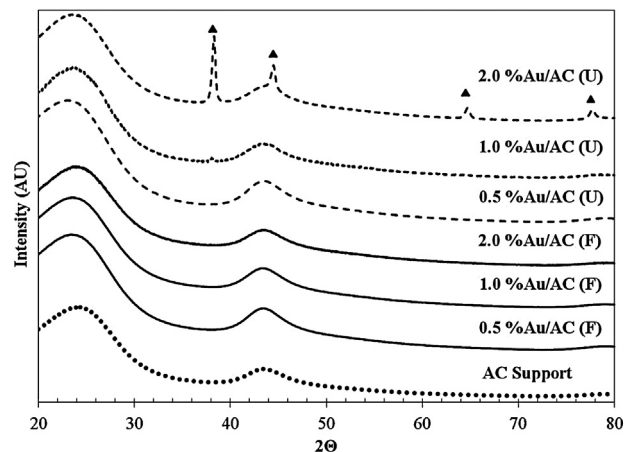

Fig. 6. XRD spectra of different gold loading catalysts before and after reaction. (F: fresh catalyst, U: used catalyst). The black triangles on plot denote principle reflections for Au^0.
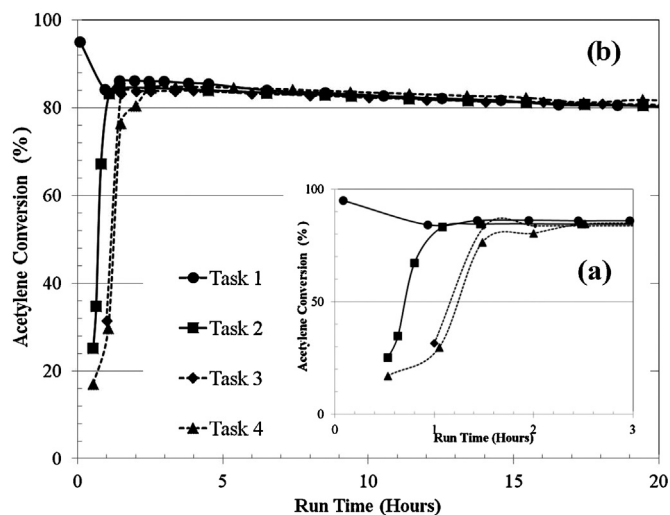
Fig. 7. Effect of pretreatment sequence on initial and longer term evaluation for acetylene hydrochlorination. The inset (a) shows initial performance from 0–3 h, and performance over the 20 h period of evaluation is shown in (b). (T = 180 °C, P = 1 atm, HCl: C_2H_2: He feed composition = 1.1: 1: 1 and GHSV = 1480 h^{-1}).
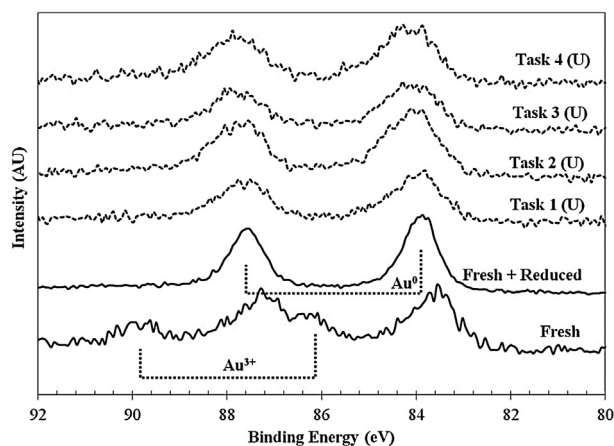

Fig. 8. XPS spectra showing Au 4f binding energies of the different catalysts after reaction (U) and comparison to XPS spectrum of fresh catalyst with no pretreatment.

oxidizes the Au metal to form the same active Au–Cl$_y$ species as during the pre-chlorination step [25]. The XPS characterization of the different catalysts after reaction (Fig. 8) confirms that only Au^0 existed during reaction, suggesting that the active Au surface is essentially metallic Au upon which a Cl-containing species is chemisorbed. While the prechlorination step can provide more active Au sites for higher initial activity for acetylene hydrochlorination, the sites are not stable for longer term operation.

4. Conclusion

The paper compares catalytic performance for acetylene hydrochlorination of Au/C catalysts prepared by different methods; ultrasonic-assisted (UL), microwave-assisted (MW), and conventional incipient wetness impregnation (CI) techniques. Acetylene conversions greater than 80% with VCM selectivity of 99.5% after 20 h reaction period can be achieved from catalysts prepared by the ultrasonic-assisted technique. This method is more preferable

than MW in terms of catalyst stability. The experimental results for 0.5, 1.0, and 2.0 wt% Au show that the catalyst activity does not depend significantly on Au loading. A loading of 1.0% Au gives the best balance of resistance to sintering and highest concentration of active Au surface sites. From the investigation on the effect of pretreatment, pre-chlorination of the catalyst prior to the reaction does promote initial, higher catalytic activity, but the long-term activity was almost identical to the other pretreatment methods, including no pretreatment before evaluation. These results indicate that the presence of Au^{3+} on the catalyst surface does give the highest initial catalyst activity while the completely-reduced Au/C on surface has the lowest initial activity. However, after an initial period of approximately five hours, activities are similar regardless of pretreatment. XPS analysis after 20 h of reaction shows the existence of only Au^0 species. In combination the results suggest that the active Au surface is essentially metallic Au upon which a Cl-containing species is chemisorbed which reacts with acetylene to form VCM.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.01.043.

References

[1] Y. Saeki, T. Emura, Prog. Polym. Sci. 27 (2002) 2055–2131.
[2] J. Zhang, N. Liu, W. Li, B. Dai, Front. Chem. Sci. Eng. 5 (2011) 514–520.
[3] S.A. Mitchenko, E.V. Khomutov, A.A. Shubin, Y.M. Shul'ga, J. Mol. Catal. A 212 (2004) 345–352.
[4] G. Hutchings, D. Grady, Appl. Catal. 17 (1985) 155–160.
[5] G. Hutchings, Catal. Today 72 (2002) 11–17.
[6] G. Hutchings, Top. Catal. 48 (2008) 55–59.
[7] G. Hutchings, Gold Bull. 37 (2004) 3–11.
[8] B. Nkosi, N. Coville, G. Hutchings, M. Adam, J. Friedl, F. Wagner, J. Catal. 128 (1991) 366–377.
[9] M. Conte, A. Carley, C. Heirene, D. Willock, P. Johnston, A. Herzing, C. Kiely, G. Hutchings, J. Catal. 250 (2007) 231–239.
[10] T. Masaharu, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, Chem. Eur. J. 11 (2005) 440–452.
[11] P. Zhang, B. Zhang, R. Shi, Front. Environ. Sci. Eng. China 3 (2009) 281–288.
[12] L. Rastogi, J. Arunachalam, J. Green Nanotechnol. 4 (2012) 163–173.
[13] H. Wu, P. Cao, W. Li, N. Ni, L. Zhu, X. Zhang, J. Alloys Compd. 509 (2011) 1261–1265.
[14] V. Belova, H. Möhwald, D. Shchukin, Langmuir 24 (2008) 9747–9753.
[15] Z. Chen, H. Li, L. Wang, J. Nat. Gas. Chem. 12 (2003) 139–144.
[16] B. Nkosi, N. Coville, G. Hutchings, Appl. Catal. 43 (1988) 33–39.
[17] W.Wittanadecha, N. Laosiripojana, A. Ketcong, N. Ningnuek, P. Praserthdam, S. Assabumrungrat, Eng. J. (accepted).
[18] N. Aldea, P. Marginean, V. Rednic, S. Pintea, B. Barz, A. Gluhoi, J. Optoelectron. Adv. Mater. 9 (2007) 1555–1560.
[19] M. Jia, H. Bai, Z. Tu, Y. Shen, Y. Li, J. Rare Earths 26 (2008) 528–531.
[20] D. Briggs, M.P. Seah, Practical Surface Analysis, vol. 1, 2nd ed., John Wiley and Sons, New York, 1993.
[21] M. Conte, C. Davies, D. Morgan, T. Davies, D. Elias, A. Carley, P. Johnston, G. Hutchings, J. Catal. 297 (2013) 128–136.
[22] C. Kumar, M. Karim, M. Joardder, J. Food Eng. 121 (2014) 48–57.
[23] A. Patist, D. Bates, Innov. Food Sci. Emerg. Technol. 9 (2008) 147–154.
[24] S. Wang, B. Shen, Q. Song, Catal. Lett. 134 (2010) 102–109.
[25] B. Nkosi, M. Adam, N. Coville, G. Hutchings, J. Catal. 128 (1991) 378–386.