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Article

Synthesis of Au/C Catalysts by Ultrasonic-Assisted Technique for Vinyl Chloride Monomer Production

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Abstract. In the present work, the ultrasonic-assisted technique is applied to synthesize Au/C catalysts for vinyl chloride monomer (VCM) production via acetylene hydrochlorination. The catalytic performance of the obtained catalysts is compared with that of the catalyst prepared by a conventional incipient wetness impregnation technique. It was found that all the prepared catalysts show high VCM selectivity (>99.5%). The use of the ultrasonic-assisted technique can significantly improve the catalytic activity and stability of the synthesized Au/C catalysts. An ultrasonic driven time of 6 hours is found to be a promising catalyst for commercial application regarding the catalyst stability. In addition, the effect of operating parameters is investigated. Suitable operating temperature and HCl/C_2H_2 feed ratio are 180°C and 1.1, respectively.

Keywords: Ultrasonic-assisted technique, acetylene hydrochlorination, vinyl chloride monomer, gold catalyst.

1. Introduction

Polyvinyl chloride (PVC) is one of the most widely-produced plastics. Its demand is continuously increasing worldwide. The volume of PVC world market reached 34 million tons in year 2008. Moreover, the PVC demand is expected to be totally more than 40 million tons in the year 2016 [1]. PVC is commercially produced from polymerization of vinyl chloride monomer (VCM), which is manufactured industrially via dehydrochlorination of dichloroethane (ethylene-based process) or hydrochlorination of acetylene (acetylene-based process). In China, the PVC capacity has increased more than 20% annually since 2000 and become greater than USA since 2005, becoming the first rank worldwide. Currently PVC production through the acetylene-based process accounts for about 70% of the total PVC production capacity in China [2]. In commercial acetylene-based process, acetylene gas reacts with anhydrous hydrochloric gas over mercuric chloride supported on activated carbon 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 arisen from sublimation of mercuric chloride during the production. This does not only affect catalyst deactivation but also cause severe safety and environmental problems [6].

Many researchers have made efforts to investigate new alternative mercuric-free catalysts for acetylene hydrochlorination. Various mercuric-free liquid catalysts such as Cu^+, Au^{3+}, Pd^{2+} and Pt^{3+} have been investigated. Pt^{3+} and Pd^{2+} complexes in solution show high activity but they are very unstable [7]. For solid catalysts, gold-based catalyst has been considered as a promising catalyst to replace the mercury-based catalysts among various metal salts i.e., Au^{3+} [5, 8, 9], Cu^{2+} [10], Pd^{2+} [11], Pt^{2+} [12, 13] and Bi^{3+} [14]. However, their performance is not satisfactory for commercial production due to stability problems. Many researchers indicated that the carbon-supported gold catalyst offers high initial activity; however, it is highly deactivated because the distribution of gold on the support is not well [15-17]. Generally, the gold catalysts have been synthesized using incipient wetness impregnation method. The disadvantage of this preparation is the low active site dispersion the gold active species which can easily aggregate during reaction condition. For the ultrasonic-assisted technique, the ultrasonic wave can enhance good mass transport, emulsification, thermal heating and variety of physical effects on the solids through cavitation phenomena. Then the local temperature and pressure may greatly change the catalyst characteristics; for example, the particle diameter may be decreased, the surface area may be increased and the atom arraangent on the crystal surface of the active substance could be out of order [18, 19]. Therefore, the ultrasonic wave is usually applied to cleaning process; however, many researches have come through investigation on applicatoin of the ultrasonic-assisted technique to improve catalyst properties [20-22].

In the present work, Au/C catalysts with high metal dispersion were synthesized by ultrasonic-assisted technique, and their catalytic activity toward the acetylene hydrochlorination was studied and compared to the catalyst prepared by typical incipient wetness impregnation technique.

2. Experimental

2.1. Catalyst Preparation

Au/C catalyst was firstly prepared by conventional incipient wetness impregnation technique using aqua regia as a solvent [23]. The activated carbon support (coconut shell based and supplied by Carbokarn) was initially washed with dilute aqueous HCl (1M) (Qrec HCl 37%) to eliminate impurities of acetylene hydrochlorination such as Na or Fe. The activated carbon support was cleaned up and filtered by distilled water and dried overnight at 110°C in an oven. A solution of $HAuCl_4 \cdot xH_2O$ (Sigma-Aldrich: 50% gold assay) in aqua regia solvent (mixture of HCl (Qrec HCl 37%): HNO_3 (Qrec HNO3 67%) = 3:1) was added dropwisely to the acid-washed activated carbon under stirring. Then the doped catalyst was dried overnight at 110°C in the oven (CI sample). Alternatively, the ultrasonic wave was applied to the catalyst synthesis during the active species doping step. The $HAuCl_4$ solution and prepared activated carbon support were mixed by ultrasonic wave in an ultrasonic bath (Crest Ultrasonic Model: 275HTAE 42-45 kHz) controlled at 45-50°C for a given driven time. Then the doped catalyst was dried overnight at 110°C in the oven (UL sample).

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 using a SIEMENS D5000 X-ray diffractometer, using a Cu K α radiation source with a nickel filter, for 2θ angles ranging from 20° to 80°. Temperature-programmed reduction (TPR) was used to determine the reduction temperature of Au^{3+}. This analysis was carried out using a Micromeritics Chemisorb 2750 pulse chemisorption analyzer, with 10% H_2 in Ar as a reducer and a temperature ramp of 30 to 400°C (ramp rate = 10°C/min, flow = 50 ml/min and held at final temperature for 30 min at 400°C)[24].

2.3. Catalytic Performance Evaluation

The catalytic performance of Au/C catalyst on acetylene hydrochlorination was tested in a fixed bed reactor (i.d. = ¼ inch). Anhydrous hydrogen chloride gas (99.999%) was dried using 5A molecular sieve column, while the acetylene gas (99.99%) was pretreated by molecular sieve 13X to remove major inhibition impurities (i.e. acetone and moisture). At the starting of the experiment, the reactor containing the catalyst was dried using nitrogen supplied at 120°C for 30 min and was then activated with a mixture of nitrogen and hydrogen chloride at a temperature of 160°C for 1 hour. Then the catalyst bed was heated up to a desired temperature under diluted HCl flow at reaction concentration. A mixture of acetylene and hydrochloride was then fed with a molar ratio of 1:1.1 for a period of 3hours. The exit gas from the reactor was passed through a sodium hydroxide solution to eliminate any unreacted hydrogen chloride gas. The gaseous products were analyzed using an on-line Shimadzu GC2014 gas chromatography with a flame ionization detector equipped with an RTX alumina column. Acetylene conversion and VCM selectivity were calculated from mass balances. The conversion was calculated as the ratio of the amount of remaining acetylene divided by the amount of feed acetylene.

3. Results and Discussion

Generally, the gold catalysts used in this reaction have been synthesized using incipient wetness impregnation method. Our previous work [23] demonstrated by TEM measurements that the CI sample has poor metallic dispersion on catalyst whereas the UL sample has excellent metallic. Typically, the properties of catalysts and their activities are in close relationship to the degree of metal dispersion. Thus, enhancing dispersion of Au catalyst on activated support should improve the catalytic performance. In this study, the amount of gold loading on catalyst is controlled at 1% wt Au/C, following the literatures [8, 15] and the effect of ultrasonic driven time of the UL catalyst synthesis on catalyst characteristics (measured by XRD and TPR) and catalytic activity of the acetylene hydrochlorination reaction is determined and compared with those of the catalyst prepared by using conventional impregnation method.

The results of X-ray diffraction (XRD) patterns of CI and UL samples at various driven times are shown in Fig. 1(a). The results show that all of fresh CI and UL samples have the XRD patterns similar to pure carbon support (CK sample) as the crystalline of Au^{3+} cannot be detected by this technique or with insignificant Au^0 reflection detectable [24]. However, the XRD spectra of used catalysts are found the peaks of Au^0 reflection. The results can confirm that one reason of catalyst deactivation phenomena is the reduction of gold active species from Au^{3+} to Au^0 as shown in Fig. 1(b). In the Au/C catalysts, the typical peaks of Au^0 were observed at 2θ = 38.2, 44.4, 64.7 and 77.7 degree, those peaks were assigned to the diffraction lines of [111], [200], [220] and [311] planes of gold [25].
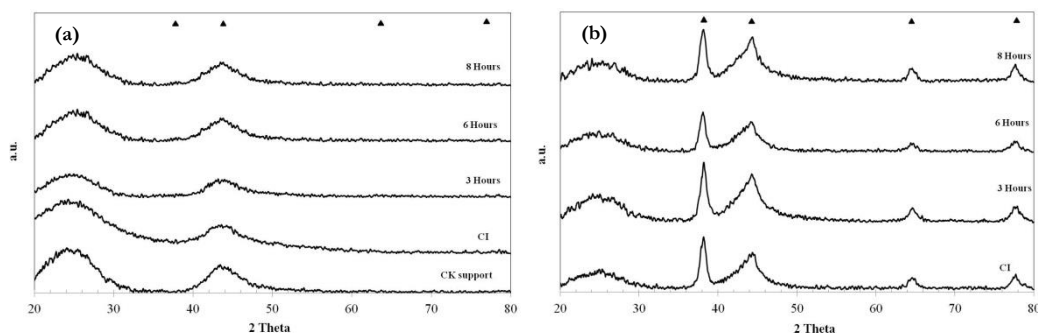
Fig. 1.   X-Ray Diffraction (XRD) spectra of different driven time ultrasonic-assisted samples compared with pure carbon support (CK support) and conventional impregnation (CI). The fresh and used catalysts XRD spectra are shown in figure (a) and (b), respectively. (The triangle represents the Au^0 XRD peak position) [25]

Figure 2 shows the temperature programmed reduction (TPR) results of CI sample and UL samples with various driven times. The reduction temperature peaks of Au/C of the UL samples are lower than the CI sample (280°C). Among the UL samples, the catalyst with 6 hours driven time shows the lowest temperature reduction (around 230°C). Generally, the temperature reduction peak is represented the reduction ability of solid catalyst. This should indicate that the opportunities of Cl$^-$ supply of the UL samples are better than the CI sample [25]. This hypothesis will be confirmed by catalytic performance results.
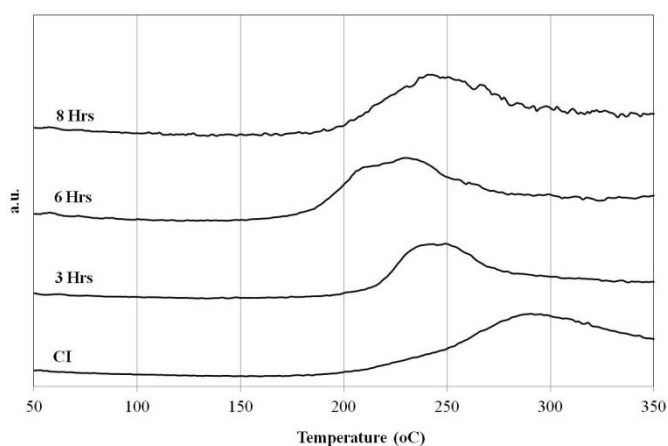

Fig. 2. H_2-TPR profiles of gold catalysts synthesized by ultrasonic-assisted technique.

The catalytic performance results of UL samples with different ultrasonic driven times and comparing with CI sample are shown in Fig. 3. The bars represent the differential percentage of acetylene conversion between the first and the third hour operation when the dashed-line bar is the first hour acetylene conversion and the solid-line bar is the third hour data. Moreover, the line shows the average deactivation rate for the reaction period of 3 hours. The results show that the initial acetylene conversion (first hour) of the sample of three hours driven time is highest while the sample of six hours driven time shows the lowest deactivation rate. However, the values are still better than that of the CI sample. These results are related with the reduction temperature results shown in Fig. 2. This relationship can be confirmed by the proposed mechanism from Wang et al.; 2010 [26], who revealed that C_2H_2 complex adsorbed on gold active species via Eley-Rideal mechanism reacts with hydrogen chloride in gas phase to produce vinyl chloride monomer. Thus, the catalyst performance is related with abilities of supplying Cl$^-$ from catalyst or reduction ability as related with TPR results in Fig. 2. From the point of view of commercial operation, the catalyst stability is the most important parameter. Thus, the six hours driven time is the suitable time for catalyst preparation by ultrasonic-assisted technique. Again, the stability of the UL samples is better than that of the CI sample. The ultrasonic wave was reported to help homogeneously distribute metal inside the porous material with narrow size distribution [27]. This can be confirms the superior catalytic performance of Au/C achieved by

the use of the ultrasonic-assisted technique for catalyst preparation. However, the acoustic cavitaion phenomena cause higher surface area but it can accelerate free radicals to oxidize the metal surface by formation of a thin oxide layer [28]. Hence, the catalysts can lose the Cl- radicals during cavitation.

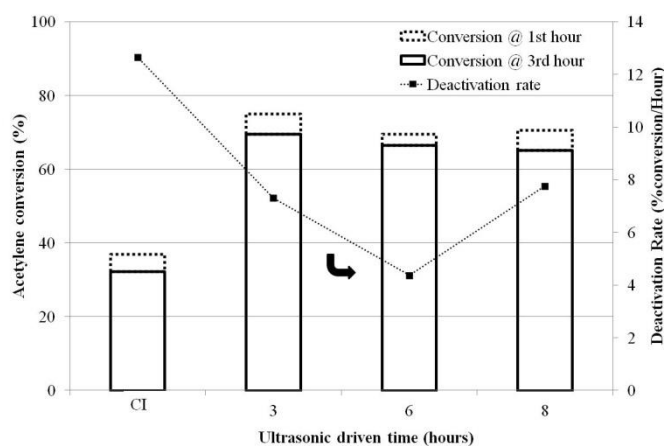Fig. 3. %Acetylene conversion of samples prepared by using various ultrasonic driven times and comparing with CI sample ($T = 180$°C, ambient pressure and HCl/C_2H_2 ratio = 1.1).

Figure 4 shows the effect of operating temperature on the acetylene conversion. Commercially, the reactors packed with mercury-based catalyst are operated at a milder condition of 130-180°C because the sublimation of mercuric active species becomes significant at temperature above 180°C [29]. In this study, three temperature levels of 160, 170 and 180°C are considered. The results indicate that the operation at $T=180$°C shows the best catalytic activity. For operation at $T = 160$ and 170°C, very low initial activities are observed; however, they progressively increase with reaction time. The change in catalytic activity with time is likely to be due to the change in size of gold catalyst by sintering. It was reported earlier that there is an optimum size of gold to catalyze the reaction [23, 30].
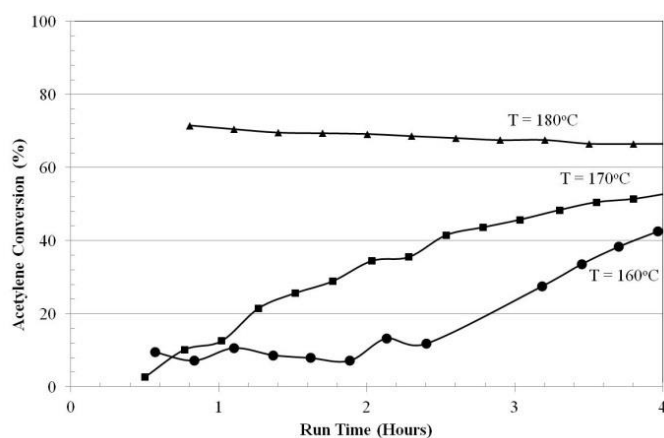

Fig. 4. Effect of reaction temperature on % acetylene conversion for catalyst prepared with 6 hours driven time (ambient pressure).

Figure 5 shows the catalytic performance for various HCl/C_2H_2 feed ratios. The results indicate that increasing HCl/C_2H_2 could increase conversion and decrease deactivation rate. The order of catalyst deactivation rate is 0.4 > 0.7 > 1.1 HCl/C_2H_2 feed ratio while the initial activity of all catalysts are almost similar. Initially, the Au/C catalyst is fulfilled chloride ion then it will be lost chloride ion from active species during reaction and regenerated by HCl in feed stream. This is because C_2H_2 acts as the reductive or deactivated substance whereas HCl plays an oxidative or regenerating role [17]. However, the excessive HCl in feed is undesirable as it would demand significant effort to remove the unreacted HCl in the downstream process. It was recommended to operate the reaction at a ratio less than 1.5 [15, 25]. In addition, further works to study catalyst regeneration by using aqua regia solution or HCl/Cl_2 on-line gas would help explore the reusability of the Au/C catalyst.
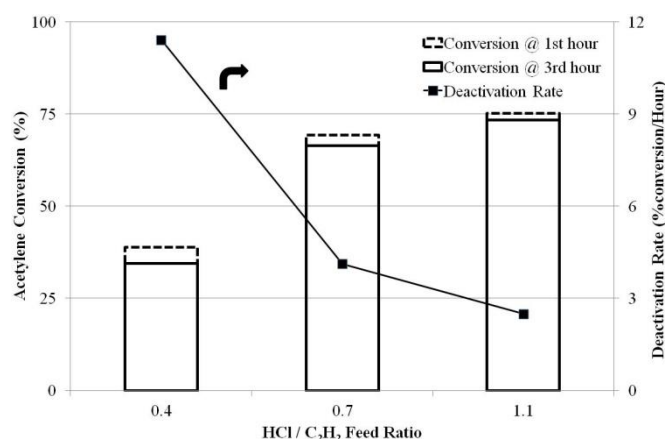
Fig. 5.   Effect of HCl/C_2H_2 feed ratio on % acetylene conversion and % VCM selectivity at steady state ($T = 180$°C and ambient pressure).

4. Conclusion

The performance of gold catalyst supported on activated carbon for acetylene hydrochlorination could be improved by changing the catalyst synthesis technique. It was demonstrated that the use of ultrasonic-assisted technique could alter the reduction ability of the catalyst. The higher catalytic activity and stability can be enhanced. The suitable condition of this reaction is at reaction temperature of 180°C and HCl/C_2H_2 feed ratio of 1.1.

Acknowledgement

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