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Bimetallic Au–Sn/AC catalysts for acetylene hydrochlorination

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ABSTRACT

A series of Au–Sn/AC catalysts for acetylene hydrochlorination were prepared by an incipient wetness impregnation method and characterized by BET, XPS, TEM, TPR, XRD, ICP-AES and TPD techniques. It is indicated that Au1Sn1/AC catalyst shows the highest activity and stability with the 95% acetylene conversion after 48 h reaction under the conditions of 170 °C and an acetylene gas hourly space velocity of 720 h^{-1}. The Sn additive can make the Au species dispersed well and weaken the occurrence of coke deposition, as well as inhibit the reduction of Au^{3+} to Au^0, thereby improving the catalytic activity and stability.

Introduction

Polyvinyl chloride (PVC) is one of the five widely used engineering plastics. In recent years, with the rapid development of the global world, the demand of PVC increases dramatically [1]. It was reported that the PVC world market reached a total volume of 34 million tons in 2008, while PVC demand was expected to be more than 40 million tons in 2016 [2,3]. Vinyl chloride monomer (VCM) is a main raw material to produce PVC. There are two common ways, including acetylene hydrochlorination and the ethylene oxychlorination, to synthesize VCM [4]. The relative shortage of oil resource results in the rapid development and growth of coal-based acetylene hydrochlorination, in which the common catalyst is $HgCl_2$/AC [5]. Mercury is highly toxic and easily volatile, and it may cause serious harm to both workers and the environment [6–8]. At the same time, the emission of mercury is forbidden by the UN Environment Programme's Governing Council in the near future [9]. Therefore it is urgent to explore an effective non-mercury catalyst for the sustainable development of PVC production.

Hutchings et al. carried out the pioneering works to study the catalysts for acetylene hydrochlorination and found that Au-based catalyst was the most promising alternative catalyst to mercuric chloride [6,10–14]. However, Au-based catalyst still faces up to significant challenges for industrial applications owing to its high cost and the poor long-term stability. To reveal the deactivation reason of Au-based catalyst, Zhang et al. [15] performed the theoretical simulation to explain the deactivation reasons of Au-based catalyst, and concluded that the difficulty of the desorption of chlorovinyl species from the active Au sites and the loss of Cl atoms can cause the deactivation of Au-based catalyst. In addition, Hutchings et al. [16,17] found that the deposition of carbonaceous material and the reduction of Au^{3+} were the two main reasons for the deactivations of Au-based catalysts. To improve the catalytic activity and stability of Au-based catalysts, the effects of other metallic component additives, involving Cu [18], La [19], Co [20], Ni [21], Bi [22], Cs [23], Pd [13,24], Ba [25], have been studied extensively. In particular, Zhang et al. [25] reported that the Ba(II) additive could inhibit the occurrence of coke deposition on the catalyst surface and inhibit catalyst sintering, with the least amount of coke deposition of 2.9% on Au1Ba(II)1/AC under the reaction conditions of 200 °C, the $V_{HCl}/V_{C_2H_2}$ ratio of 1.15, the acetylene gas hourly space velocity (GHSV) of 360 h^{-1} and the reaction time of 48 h. However, it is still a challenge so far to explore an effective additive that can reduce the amount of coke deposition but also inhibit the reduction of Au^{3+}.

Sn is always used as a promoter to improve the catalytic activity and prolong the life of catalyst. During the dehydrogenation of light alkanes, the addition of Sn can change the particle size of Pt and promote the positive charge transfer from Sn^{n+} to Pt, which can inhibit the reaction of coking, thus improving the catalytic activity and stability [26–32]. In the case of methanol oxidation, the process was facilitated by tin oxides which can supply more oxygen atoms to an adjacent site [33,34], and the bimetallic Pt–Sn

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catalyst showed much better catalytic performance. We are inspired to study whether or not the Sn additive can enhance the catalytic performance of Au-based catalysts for acetylene hydrochlorination.

In this article, we synthesized a series of Au–Sn/AC catalysts and studied the effect of Sn additive on the catalytic performance of Au/AC catalysts for acetylene hydrochlorination. The catalysts were characterized by BET, XPS, TEM, TPR, XRD, ICP-AES and TPD. The results here indicated that the appropriate amount of Sn could make the Au species dispersed well and inhibit the coke deposition on the catalyst surface, consequently improving the activity and stability of Au-based catalysts.

Experimental

Materials

$HAuCl_4 \cdot 4H_2O$ (Au content $\geq$47.8%) was purchased from Alfa Aesar company; $SnCl_2 \cdot 2H_2O$ was purchased from Tianjin Guangfu Technology Development Co., Ltd., and AC (pH = 5–7, cocoanut shell carbon) was purchased from Fujian S.S. Activated Carbon Industry Science and Technology Co., Ltd. All the other materials and chemicals were commercially available and were used without further purification.

Catalyst preparation

Bimetallic Au–Sn/AC catalysts (425–830 μm) were prepared using an incipient wetness impregnation technique with the precursors of $SnCl_2 \cdot 2H_2O$ and $HAuCl_4 \cdot 4H_2O$. The raw material of cocoanut shell-based activated carbon was pretreated by 0.01 mol L^{-1} HCl aqueous solution at 70 °C for 5 h to remove impurities, followed by water washing to neutral pH value and then dessication at 120 °C for 24 h under vacuum; the obtained clean activated carbon was denoted as AC and used as the catalyst support. To prepare the Au–Sn/AC catalysts, a $SnCl_2$ solution with pH value of 2 was first added dropwise to the activated carbon support under stirring, followed by the incubation at room temperature for 12 h. After the evaporation 60 °C for 16 h, the obtained mixture was impregnated quantitatively by a $HAuCl_4$ *aqua regia* solution under stirring. Experienced the similar incubation and evaporation period, the bimetallic Au–Sn/AC catalysts were obtained with different Au/Sn molar ratios after the dessication at 150 °C for 18 h. The Au loading amount of all the catalysts was fixed at 1 wt%, and the bimetallic catalysts were denoted as Au1Sn*x*/AC with the molar ratio *x* of 0.5, 1, or 3. As a control, the monometallic catalyst Au/AC (1.0 wt% Au) and Sn/AC (0.6 wt% Sn) catalysts were also prepared through the similar procedures described above. The actual contents of Au and Sn in the fresh catalysts have been determined by ICP-AES (Table S1). The total Au contents in Au/AC-fresh, Au1Sn0.5/AC-fresh, Au1Sn1/AC-fresh and Au1Sn3/AC-fresh catalyst are 0.910 wt%, 0.908 wt%, 0.911 wt% and 0.912 wt%, respectively.

Catalyst characterization

The specific surface area and total pore volume of the catalysts were measured by low-temperature N_2 adsorption/desorption experiment at −196 °C with a volumetric adsorption system (Quantachrome Instruments). All catalysts were degassed at 300 °C for 4 h prior to the analysis.

The crystallinities of the samples were analyzed by X-ray powder diffraction spectra (XRD, Rigaku D/MAX-2500, Japan) with Cu Kα radiation at a scanning rate of 8° min^{-1} for 2θ degree ranging from 10° to 90°.

Surface chemical compositions and the valence states of elements were determined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xl), using a monochromatised Al Kα X-ray source (225 W), with the minimum energy resolution of 0.45 eV (Ag $3d_{5/2}$) and the minimum XPS analysis area of 3 μm. Binding energies were calibrated by the C1s binding energy of carbon, 284.8 eV.

The coke deposition of the catalysts was analyzed by a thermogravimetry/differential thermal analysis (TG-DTA) instrument (Mettler Toledo TGA/SDTA851e, Switzerland) from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in an air flow of 50 mL min^{-1}.

The reducibility and the adsorptive property of the catalysts were measured by temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments using an AutoChem BET TPR/TPD (Quantachrome Instruments AMI-90). The weight of all samples for TPR and TPD experiments was 100 mg. For TPR experiment, the sample was heated from room temperature to 800 °C at a rate of 10 °C min^{-1}, flushing with a 20 mL min^{-1} gas mixture containing 6 vol% H_2 in Ar. The desorption of moisture was performed at 200 °C for 120 min before the TPD experiment. For C_2H_2 and C_2H_3Cl TPD experiment, the adsorption of samples experiment was performed at 90 °C for 30 min, flushing with a 20 mL min^{-1} pure C_2H_2/C_2H_3Cl gas. After the adsorption, the samples were treated with pure helium gas at 90 °C for 60 min and then cooled to the room temperature. After that, the desorption was performed from 30 to 600 °C at helium atmosphere. For the HCl-TPD experiment, the process was the same as that of C_2H_2- or C_2H_3Cl-TPD, except of an injector used to input HCl sample. The total injection volume of HCl was 3000 μL.

The morphologies of catalysts were observed by transmission electron microscopy (TEM, JEM-2100F). The samples were dispersed in ethanol and supported on carbon-film-coated copper grids before the characterization of TEM.

Calculation models and method

Previous work has proved that in the Au-based catalyst the active species should be the dimer of $AuCl_3$, i.e., Au_2Cl_6 [15]. And other two kinds of dimers involving Au_2 and Au_2Cl_2 are also studied as the models of Au^0 and Au^+ species in the DFT calculations [35,36]. Thus, we adopted Au_2Cl_6 and Au_2 as the models of active sites to study the adsorption energy of VCM through density functional theory (DFT) calculations.

All of the DFT calculations were performed by Dmol^3 code of Materials Studio software from Accelrys Inc. In the geometrical optimization of the catalysts and VCM, the a-spin-polarized revised Perdew–Burke–Ernzerhof (RPBE) [37] functional within the formulation of the generalized gradient approximation (GGA) and a double-numerical basis set with polarization functions (DNP) were selected [38]. All electron relativistic core treatment was used in all of the calculations. All the structures were optimized without any constraint. The energy convergence criterion was chosen as 0.0003 eV. In order to speed up the convergence of self-consistent field, a thermal smearing of 0.136 eV was applied to the orbital occupation.

The adsorption energy (E_{ad}) is defined as below:

$$E_{ad} = E_{ad\text{-}state} - (E_{VCM} + E_{catalyst}) \quad (1)$$

where $E_{ad\text{-}state}$ is the total energy of the VCM-catalyst systems, while $E_{catalyst}$ and E_{VCM} are respectively the total energy of the relaxed single catalyst and the VCM in the gas phase. A negative value of E_{ad} indicates that the adsorption process is energetically favorable. The more negative of E_{ad}, the stronger adsorption of VCM on the catalyst.