



Short communication

Enhanced stability of hydrochlorination of acetylene using polyaniline-modified Pd/HY catalysts



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ABSTRACT

A polyaniline (PANI)-modified zeolite Y supported Pd catalyst (Pd/PANI-HY) for acetylene hydrochlorination was successfully synthesized by ultrasonic-assisted impregnation. The catalyst exhibited excellent stability, and acetylene conversion was maintained at >95% more than 300 h. The excellent stability of the Pd/PANI-HY catalyst was attributed to the presence of the polyaniline that partly weakens the occurrence of carbon deposition and also inhibited the reduction of the Pd²⁺ active component on the catalyst surface.

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1. Introduction

Acetylene hydrochlorination is an important industrial route to synthesize vinyl chloride monomer (VCM) [1–2]. However, the HgCl₂ catalyst used for acetylene hydrochlorination is highly toxic and causes serious environmental pollutions. In addition, Hg resources are in short supply [3]. Therefore, exploring non-mercury catalysts in acetylene hydrochlorination reaction becomes highly imperative [4–6].

So far, several noble metal catalysts (involving Au, Pd, Pt, Rh, Ir, Ru) supported on active carbon [4–19] have been studied for the acetylene hydrochlorination, since Hutchings [4] suggested that the activity of the metal catalyst was correlated with the standard electrode potentials of the metal ions. Thereafter, the extensive work has demonstrated that Au was the most active for the hydrochlorination of acetylene and Au³⁺ was the active component in Au-based catalysts [4]. However, the present Au catalyst is still unstable and easily deactivated with the reaction time due to the Au reduction, the surface carbon deposition, the pulverization of solid catalyst, etc. [9–11]. In the reaction, acetylene is the electron donor and hydrogen chloride is the electron receptor, hence, when the reactants are absorbed on the active sites, Au³⁺ obtains the electron of acetylene and is reduced readily to Au⁰ under reaction conditions and consequently loses its activity [16]. In order to improve the

catalytic performance of metal catalysts, several efforts have been made, such as adding the second metallic components (La, Co, Ni, Ba, K, etc.) [10–14] or choosing the appropriate supports (SiO₂, TiO₂, Al₂O₃, zeolites, CNTs, etc.) [17–22]. On the one hand, the catalytic performance of catalysts affected by the second metallic components is attributed to changes in the electronic structure of the active metal, due to electron-transfer between the active component and another metal chloride [10–14]. On the other hand, the metal-support interaction affected by the different supports (including modified-supports) is attributed to the electron density of active components, which can improve the catalyst activity [17–19]. In previous work [20–22], we have shown that supported Pd catalysts over HY zeolites can be applied for acetylene hydrochlorination. The Pd-based catalysts with NH₄F modification had an enhanced stability related to changes of the surface acidity, less carbon deposition and Pd loss, but their lifetimes were short and the variation of Pd valence states was not discussed during the reaction [22]. In addition, many literatures have reported that the N-containing supports played an important role in the reduction of metals and the metal-support interaction [18,23–24], which could enhance the catalytic performance of catalysts for acetylene hydrochlorination. Therefore, these results have prompted us to investigate the nitrogen-modified Pd/HY catalysts in the acetylene hydrochlorination reaction. In this paper, we reported a novel non-mercury hydrochlorination catalyst that employs polyaniline to promote Pd/HY catalyst in stability. Through characterizations, it is indicated that the presence of the polyaniline can significantly influence the occurrence of carbon deposition and the palladium reduction, and over Pd/4PANI-HY catalyst the

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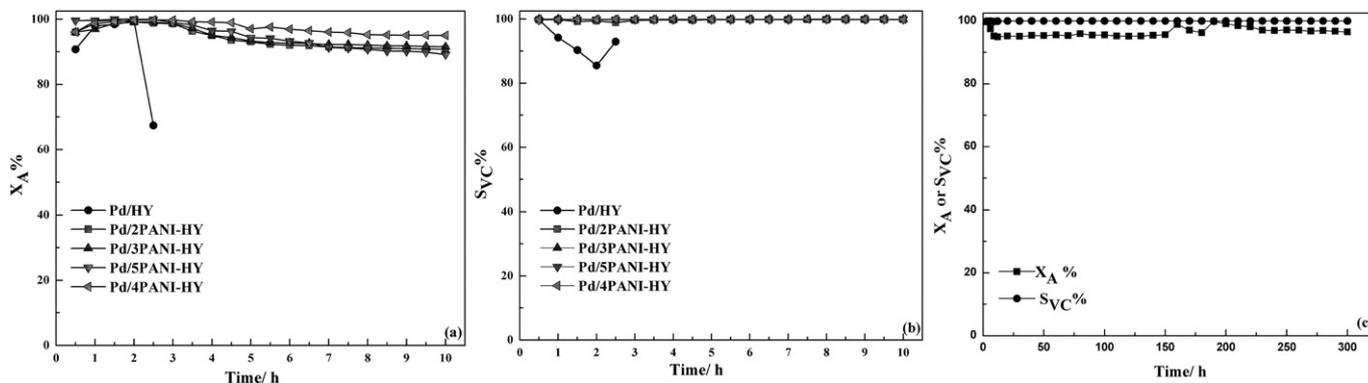


Fig. 1. The C_2H_2 conversion (X_A) and the selectivity to VCM (S_{VC}) over Pd-based catalysts; reaction condition: temperature = 160 °C, feed volume ratio $V_{HCl}:V_{C_2H_2} = 1.25$, C_2H_2 GHSV = 110 h^{-1} .

acetylene conversion keeps above 95% with 300 h on stream under 160 °C and $GHSV(C_2H_2) = 110 h^{-1}$.

2. Experimental

2.1. Preparation of the catalysts

PANI-HY supports were synthesized via an in situ oxidative polymerization [25], in which the nature zeolite was Si/Al = 9 purchased by Nankai University. HY zeolites (4.0 g) were stirred in 100 mL of 2 mol/L HCl by ultrasonic agitation for 30 min at room temperature. Aniline (CP, >98%, 4 mL), ferrous sulfate solutions (5%, 1 mL) and

ammonium persulfate (CP, >98%, 0.5 g/mL) were dispersed in mixtures of HCl and zeolites with continuous stirring for 1 h in an ice bath, and were kept at constant stirring for another 3 h. When the reaction was completed, the dark green precipitates (PANI species) resulting from the polymerization reaction were filtered and washed with distilled water until the water was near neutral pH. Then the precipitates were dried overnight in a vacuum oven at 80 °C. The amount of PANI species mass was varied from 20 wt.%–50 wt.%, and the obtained samples were named as 2PANI-HY, 3PANI-HY, 4PANI-HY, and 5PANI-HY, respectively.

Pd/PANI-HY catalysts were prepared by ultrasonic-assisted impregnation [20–22]. PANI-HY supports were dried at 120 °C for 1 h, and then impregnated using H_2PdCl_4 with stirring in air. The loading of Pd was kept constant at 0.9 wt.%. After impregnation, the resulting products were dispersed by ultrasonic dispersion for 1 h and kept for a night at room temperature, then dried at 80 °C for 12 h and used as catalysts.

2.2. Catalyst characterization

X-ray diffraction (XRD) data were collected on a M18XHF22-SRA diffractometer with Cu-K α irradiation in the scan range of 2θ between 10° and 80° at 50 kV, 100 mA. Samples were dried in the vacuum oven at a temperature of 343 K for 5 h and then analyzed by X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA, Kratos Analytical Ltd.) with binding energies of the C1s line at 284.8 eV. H_2 temperature programmed reduction (H_2 -TPR) was performed by using a TP-5080 adsorption instrument and the actual palladium contents were detected using an inductively coupled plasma (ICP-6300) instrument. Data from an energy dispersive spectrometer (EDS) analyzer attached to a scanning electron microscope (SEM) were recorded on a LEO1450VP experiment and transmission electron microscopy (TEM, H-600-II) was adopted to learn the dispersion of active components. Brunauer–Emmett–Teller (BET) surface area data were measured by JW-BK equipment. A thermogravimetric (TG) analysis was performed by the TG-DSC simultaneous thermal analyzer (NETZSCH SAT 449F3 Jupiter, Germany), at air atmosphere, a flow rate of 100 $mL min^{-1}$, and a heating rate of 10 °C min^{-1} . Fourier transform infrared (FT-IR) spectroscopy was performed using a Bruker EQUINOX-55 spectrometer with the sample/KBr pressed pellets.

2.3. Catalytic performance tests

Catalysts were tested for acetylene hydrochlorination in a fixed bed with a quartz tube microreactor (i.d. of 10 mm) operating just at normal pressure. N_2 flow (20 $mL min^{-1}$) was passed through calibrated mass flow controllers (Sevenstar Huachuang Electronics Co. Ltd., Beijing, China) in a heated glass reactor and then hydrochloride (20 $mL min^{-1}$) was passed through the reactor to activate the catalyst. After the reactor was heated to 160 °C, hydrochloride (12.6 $mL min^{-1}$) and acetylene (10.1 $mL min^{-1}$) were fed through a mixing vessel containing catalyst

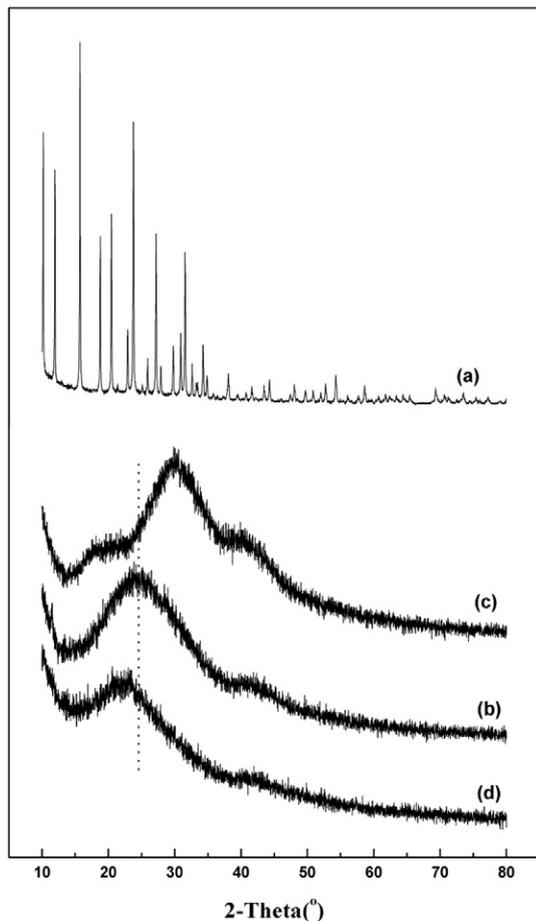


Fig. 2. XRD images of (a) HY, (b) 4PANI-HY, (c) the fresh Pd/4PANI-HY catalyst and (d) the used Pd/4PANI-HY catalyst.

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