



Short communication

Effect of K promoter on the stability of Pd/NFY catalysts for acetylene hydrochlorination

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ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form 27 February 2016

Accepted 25 April 2016

Available online 30 April 2016

Keywords:

Palladium catalysis

NFY zeolite

Potassium promoter

Acetylene hydrochlorination

ABSTRACT

Pd and Pd–K bimetallic catalysts were prepared and applied in acetylene hydrochlorination reaction. Using NFY zeolites as supports, the Pd–K/NFY catalyst showed both high activity and excellent stability, with a C₂H₂ conversion of 99% more than 50 h. Characterized results indicate that the K promoter can stabilize the Pd²⁺ species and weaken the occurrence of carbon deposition on the catalyst surface, thus improving the stability of the Pd-based catalysts.

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1. Introduction

Acetylene hydrochlorination is an important coal-based technology to synthesize vinyl chloride monomer (VCM) for the poly vinyl chloride (PVC) production [1–2]. In China, exploring non-mercury catalysts for acetylene hydrochlorination has attracted a lot of attentions recently, owing to the predicted prohibition of the application of toxic and scarce mercury chloride [3–4].

Since Hutchings et.al [5–14] found that gold-based catalysts had high activities in reaction and the coke deposition and the Au³⁺ reduction were main reasons for their rapid deactivation [13–14], most researches are focused on the Au-based catalysts [15–20] and the other noble metal-based catalysts have comparatively less reports, which also have good activities with lower cost but poor stabilities in acetylene hydrochlorination reaction [5–7,21]. Nokosi et.al [5–7] reported that the acetylene conversion rate of PdCl₂/C catalysts was higher than that of HgCl₂/C catalysts within only several hours. Song et.al [21] investigated the deactivation of Pd/C catalysts and suggested that the Pd–KCl–LaCl₃ catalyst could improve the catalyst stability for decreasing the Pd loss, but the valence changes of Pd species were not discussed. In addition, the activated carbon support has a low mechanical strength and is easily pulverized, which causes the high active component loading and difficulties in regeneration [14]. Hence, exploitation of the new support or Pd-based catalysts may be a considerable way to improve the stability and decrease the cost of Pd-based catalysts for acetylene hydrochlorination. In our previous work, it has been

demonstrated that the stability of the Pd/HY catalysts can be enhanced after modification with NH₄F or PANI and the property of zeolites support can affect the catalyst stability for acetylene hydrochlorination [22–24]. However, the stabilities of Pd-based catalysts are still inferior to the Au-based catalysts. Therefore, it is still a challenge to study the improvement of the catalytic stability for Pd-based catalysts for acetylene hydrochlorination.

In this work, aiming to improve the stability of Pd-based catalysts and develop efficient non-mercury catalysts, a series of palladium–potassium (Pd–K) catalysts were prepared and their catalytic performances were evaluated by a fixed-bed reactor. Properties of Pd-based/NFY catalysts were investigated and the effects of K on the stability of Pd-based/NFY catalysts were discussed.

2. Experimental

2.1. Preparation of the catalysts

The HY zeolites (purchased by Nankai University) were added into the 10% NH₄F aqueous solution with continuous stirring for 4 h and washed with distiller water to pH about 7. Then water was evaporated at 80 °C for 10 h and the product was denoted as the NFY support. Zeolite materials (HY, NFY, HZSM-5, H β , HMOR) supported palladium-based catalysts were prepared using ultrasonic-assisted impregnation method [22–24]. A similar method was used to prepared bimetallic Pd–K/NFY catalysts using PdCl₂ and KCl aqueous solutions as metal precursors. A PdCl₂ aqueous solution was added dropwise to the NFY support with ultrasonic wave for 1 h and set aside for a night at room temperature, followed by evaporation at 80 °C for 10 h and adding

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Table 1

Catalytic performance of Pd-based catalysts on different zeolite-based supports ($T = 160\text{ }^{\circ}\text{C}$, feed volume ratio $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2} = 1.25$, C_2H_2 GHSV = 110 h^{-1} , $t = 120\text{ min}$).

Samples	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	$X_{\text{A}}\%$	$S_{\text{VC}}\%$
HY	505	97	94
NFY	516	99	99
H β	396	63	83
HZSM-5	272	49	96
HMOR	21	45	95

quantitatively (the weight% is 3.0%, 5.0%, 7.0% and 9.0%) a KCl aqueous solution. After the mixture was impregnated and dried as above, the Pd-K/NFY catalysts were obtained and named Pd-3K/NFY, Pd-5K/NFY, Pd-7K/NFY, Pd-9K/NFY, respectively. The Pd loading in all samples was 0.9 wt%.

2.2. Catalyst characterization

BET surface areas and pore parameters were measured by JW-BK Brunauer-Emmett-Teller (BET) equipment. Thermogravimetric (TG) tests were performed by a NETZSCH SAT 449F3 multifunctional thermal analyzer in an air atmosphere at a flow rate of 50 mL min^{-1} . X-ray diffraction (XRD) data were used a M18XHF22-SRA diffractometer operating at 50 kV, 100 mA with Cu-K α irradiation in the scan range of 2θ between 10° – 80° . Palladium contents were detected using an inductively coupled plasma (ICP-6300) instrument. X-ray photoelectron spectroscopy (XPS) data were executed by AXIS ULTRA spectrometer (Kratos Analytical Ltd) and binding energies were referred to the C1s line at 284.8 eV.

2.3. Catalytic performance tests

Catalytic performance tests were evaluated in a fixed bed with 10-mm-diameter a quartz tube micro reactor. N_2 flow (20 mL min^{-1}) via calibrated mass flow controllers (Sevenstar Huachuang electronics, Co. Ltd, Beijing, China) in a heated glass reactor and then hydrochloride at a flow rate of 20 mL min^{-1} passed through the reactor to activate the catalyst. After the reactor was heated to $160\text{ }^{\circ}\text{C}$, hydrochloride (12.6 mL min^{-1}) and acetylene (10.1 mL min^{-1}) were fed through a mixing vessel containing catalyst (4.0 g), giving a C_2H_2 gas hourly space velocity (GHSV) of 110 h^{-1} . The exit gas mixture from the reactor was passed through an absorption bottle filled with sodium hydroxide solution and then set into a gas chromatography (GC 2010, Shimadzu) to analyze the acetylene conversion (X_{A}) and the VCM selectivity (S_{VC}) immediately.

3. Results and discussion

Table 1 shows the effect of Pd-based catalysts for acetylene hydrochlorination on HY, NFY, HZSM-5, H β and HMOR zeolite-based

Table 2

Pore structure parameters of samples.

Catalyst	$S_{\text{BET}}(\text{m}^2\text{ g}^{-1})$		Total pore volume ($\text{cm}^3\text{ g}^{-1}$)	
	Fresh	Used	Fresh	Used
NFY	516	/	0.32	/
Pd/NFY	170	33	0.12	0.11
Pd-3K/NFY	128	38	0.22	0.18
Pd-5K/NFY	120	36	0.24	0.11
Pd-7K/NFY	107	37	0.30	0.12
Pd-9K/NFY	101	22	0.20	0.12

supports in the same conditions. As seen from Table 1, the order of catalysts' initial activities are: Pd/NFY > Pd/HY > Pd/H β > Pd/HZSM-5 > Pd/HMOR. In addition, the stabilities of Pd/NFY and Pd/HY are better and other Pd/zeolite-based catalysts deactivate faster. Combination with the results of BET surface areas, it is shown that the Pd-based catalysts' activities are enhanced with their specific surface areas increases, which is agreed with Zhang et al. reported [15]. Compared with the Pd/HY catalyst, the catalytic performance of the Pd/NFY catalyst is enhanced due to the presence of the nitrogen and fluorine, which can change the surface acidity and reduce the carbon deposition on the surface catalysts [23].

The catalytic performance of monometallic Pd/NFY, K/NFY and bimetallic Pd-K/NFY catalysts for acetylene hydrochlorination are shown in Fig. 1. For the Pd/NFY catalyst, C_2H_2 conversion (about 99%) and VCM selectivity (about 98%) is relatively high in the reaction, but it is still deactivated from 99% to 47% after 7 h (Fig. 1a). For bimetallic Pd-K/NFY catalysts, the initial acetylene conversion is 95% over Pd-3K/NFY, 96% over Pd-5K/NFY, 99% over Pd-7K/NFY and 94% over Pd-9K/NFY, respectively, which are all higher than that of the monometallic Pd/NFY catalyst. It is clear that the Pd-7K/NFY catalyst displays the best catalytic performance with the C_2H_2 conversion of 99% and the VCM selectivity of 99% after 10 h and no visible decline in activity is observed within 50 h (Fig. 1c), which may be ascribed to more active sites being present for the high dispersion of Pd by the addition of K [18]. On the whole, the VCM selectivity over all these catalysts is greater than 98% (Fig. 1b) and K/NFY shows almost no catalytic activity in the reaction. These results also demonstrate that K can't provide catalytic activity for acetylene hydrochlorination, and it plays a role in enhancing the stability of Pd-based/NFY catalysts.

The specific surface areas and total pore volumes of the fresh and used catalysts are listed in Table 2. It is indicated that NFY had the largest surface area of $516\text{ m}^2\text{ g}^{-1}$ and total pore volume of $0.32\text{ cm}^3\text{ g}^{-1}$. After loading of Pd or Pd–K, both the surface area and total pore volume of NFY are reduced, due to the active species filling or blocking some of the pores [15,17–18]. It is clear that the specific surface areas of the fresh catalysts decrease with the K additives increases. After reaction, the used catalysts show a lower specific surface area than the corresponding fresh one and the differences of catalysts BET surface areas ($\Delta S_{\text{BET}}\%$) are in the following order: Pd/NFY (80.6%) > Pd-9K/NFY

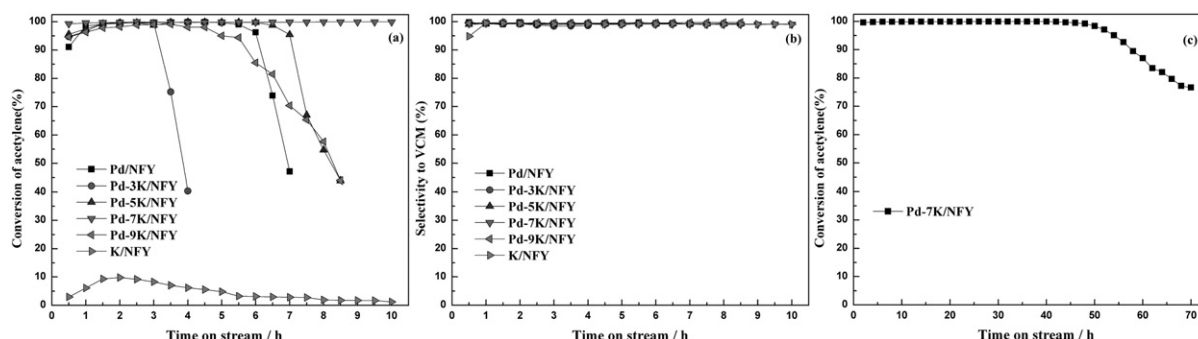


Fig. 1. Catalytic performance of bimetallic Pd-K/NFY catalysts. Reaction conditions: Temperature = $160\text{ }^{\circ}\text{C}$, feed volume ratio $V_{\text{HCl}}:V_{\text{C}_2\text{H}_2} = 1.25$, C_2H_2 GHSV = 110 h^{-1} .

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