Active ruthenium species in acetylene hydrochlorination

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ABSTRACT

A series of ruthenium-based catalysts were prepared using spherical activated carbon as a support with the treatment of oxidation or reduction. The catalytic performances of the prepared catalysts were assessed in the hydrochlorination of acetylene based on their characterisation by BET, TG, TEM, TPR, Raman, and XPS. The best catalytic performance was achieved with the oxidised catalyst Ru/SAC-C300, which exhibited a stable acetylene conversion at 96.5% in 48 h at 170 °C and a GHSV (C_2H_2) of 180 h^{-1}. It is proposed that there exist three major active sites on the surface of Ru-based catalysts for acetylene hydrochlorination, i.e., the oxidised site (RuO_2), the reduced state (metallic Ru) and the complexes of Ru/RuOy. Compared with the active ingredient of metallic Ru and Ru/RuOy through the reductive treatment, the active ingredient of RuO_2 is key for improving the catalytic performance of Ru-based catalysts through the oxidative treatment, which provides a promising route to explore high efficient non-mercuric catalysts for acetylene hydrochlorination.

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1. Introduction

Exploring non-mercury catalysts for acetylene hydrochlorination has recently attracted a lot of attention, owing to the predicted prohibition of the application of toxic mercuric chloride, the main component of industrial catalysts in some coal-based chemical production processes, by the United Nations in the near future [1–3]. Several non-mercuric catalysts, involving Au [4–9], Pd [10], Pt [11,12], have been studied in acetylene hydrochlorination, which has been enlightened by the pioneering work of Hutchings that suggested that the activities of metal catalysts were associated with the standard electrode potentials of the related metal ions [13]. However, there still remains the challenge of developing an efficient non-mercury catalyst with high activity and long stability.

Ruthenium-based catalysts have been reported to catalyse reactions including ammonia synthesis/decomposition [14], metathesis reactions [15], dehydrogenation of ethane [16], oxidation reactions [17], selective aerobic oxidation of ethanol [18] and hydrogenation of the bio-oil [19]. Depending on the individual reaction, the active ruthenium species have been proposed to be associated with RuO_x, RuO_4^{2-} [20], RuO_3 [21], RuO_2 [22] or Ru^0 [23] species. Recently, ruthenium-based catalysts were reported to be active for acetylene hydrochlorination, e.g., over Ru-Co/C catalysts, the acetylene conversion was 95% with 48 h on stream at

170 °C and a C_2H_2 hourly space velocity of 180 h^{-1} [24]. However, it still remains unclear what ruthenium species is predominant in the acetylene hydrochlorination reaction, which is the basis for improving the catalytic activity and long-term stability of Ru-based catalysts.

In this article, to determine the active ruthenium species in acetylene hydrochlorination, we prepared Ru catalysts using $RuCl_3$ as the metallic precursor and the spherical activated carbon (SAC) as the support. To adjust the types of ruthenium species, the original Ru/SAC catalysts were treated in either oxidative or reductive atmospheres at different temperatures. The catalytic performances of the oxidised, reduced and original Ru/SAC catalysts were measured in the acetylene hydrochlorination reaction. Characterisation via BET, TEM, Raman, XRD, XPS and TG indicated that there exist two distinct structures of the active ingredients in the oxidative and reductive treatments. RuO_2 is the major active ingredient in the oxidative treatment, while the metallic Ru and Ru/RuOy are the major active ingredients in the reductive treatment.

2. Experimental

2.1. Preparation of Ru-based catalysts

2.1.1. Original Ru/SAC catalysts

Spherical activated carbon (SAC) (20–40 mesh) was used as the support to prepare Ru-based catalysts via the incipient wetness impregnation method. To maintain the Ru loading content at 1 wt%, an aqueous $RuCl_3$ solution was added quantitatively into the SAC

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support at room temperature under stirring, followed by incubation at 60 °C for 12 h and was then desiccated at 150 °C for 12 h. The obtained catalyst was named Ru/SAC.

2.1.2. Oxidised Ru/SAC catalysts

The original Ru/SAC catalysts were oxidised for 1 h at high temperatures in the range of 200–400 °C and were flushed with air at a flow rate of 100 mL/min. The obtained oxidised Ru/SAC catalysts were named in terms of the temperature, i.e., Ru/SAC-C200 indicates the Ru/SAC catalysts experienced oxidation at 200 °C for 1 h, while Ru/SAC-C300 and Ru/SAC-C400 are the Ru/SAC catalysts oxidised at 300 and 400 °C, respectively.

2.1.3. Reduced Ru/SAC catalysts

The original Ru/SAC catalysts were reduced for 1 h at high temperatures in the range of 300–500 °C, under an atmosphere of 10% H_2 and 90% Ar at a flow rate of 100 mL/min. The reduced Ru/SAC catalysts were named as Ru/SAC-R300, Ru/SAC-R400 and Ru/SAC-R500, indicating the Ru/SAC catalysts that were subjected to reduction at 300, 400, 500 °C, respectively.

2.2. Catalytic performance tests

The catalytic performance tests were carried out in a fixed-bed stainless steel microreactor (i.d. 10 mm). The reactor temperature was regulated with a CKW-1100 temperature controller produced by Chaoyang Automation Instrument Factory (Beijing, China). The reaction system was first purged using nitrogen to remove water and air. The clean acetylene (15 mL/min) and hydrogen chloride (16.5 mL/min) reactants were fed into the reactor via calibrated mass flow controllers under a pressure of 1.1–1.2 bar. The reaction conditions were maintained at 170 °C, a C_2H_2/HCl feed volume ratio of 1:1.1 and a C_2H_2 gas hourly space velocity (GHSV) of 180 h^{-1}. The effluent stream of the reactor was absorbed by NaOH aqueous solution and then analysed using a Beifen 3420A gas chromatograph.

2.3. Catalyst characterisation

N_2 adsorption/desorption experiments were conducted using the ASAP 2020C surface area and porosity analyser (Micromeritics Instrument Corporation, USA), with the samples degassed at 150 °C for 5 h and analysed via liquid nitrogen adsorption/desorption at −196 °C. Transmission electron microscopy (TEM-EDX) was performed on a JEM-2010FEF instrument (JEOL, JP). To prepare the samples, the catalyst powder was dispersed in ethanol, and then, droplets of the suspension were laid and vaporised on a 300-mesh copper TEM grid with a holey carbon film. Structural deformations of the catalyst active components were determined by Raman spectroscopy (Renishaw, UK). A He–Ne laser source was used and a wavelength (λ) of 633 nm. X-ray diffraction (XRD) measurements were performed using a D8-Focus X-ray diffractometer (Bruker AXS, GER) with monochromatised Cu Kα radiation (λ = 1.5406 Å) operating in the 2θ scan range from 20º to 90º. Temperature-programmed reduction (TPR) experiments were performed using a TPDRO 1100 (Thermo-Finnigan) instrument in a micro-flow reactor fed with a 5% H_2/Ar mixture at a flow rate of 20 mL/min. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a PHI-5000 Versaprobe spectroscope (ULVAC-PHI, JP). The binding energy was calibrated with respect to the C 1s level of contaminated carbon at 284.80 eV. Thermogravimetric analysis (TGA) was performed using a TG-DSC simultaneous thermal analyser (Netzsch STA 449F3 Jupiter, GER) in an air atmosphere at a flow rate of 50 mL/min. The temperature was increased from 30 to 900 °C with a heating rate of 10 °C/min. The CO pulse chemisorption (CO-TPD) was performed using an automated chemisorption analysis instrument from Altamira (AMI-200). The sample was first reduced at

Table 1
Pore structure parameters of catalyst samples.

Catalyst	S_{BET} (m²/g)		Total pore volume (cm³/g)	
	Fresh	Used	Fresh	Used
Ru/SAC	954	827	0.58	0.48
Ru/SAC-C200	1089	1020	0.67	0.59
Ru/SAC-C300	1107	1067	0.71	0.64
Ru/SAC-C400	766	609	0.41	0.38
Ru/SAC-R300	922	871	0.59	0.51
Ru/SAC-R400	882	799	0.58	0.53
Ru/SAC-R500	867	761	0.54	0.49

400 °C for 1 h in 10% H_2/Ar at a flow rate of 40 mL/min and was then cooled to room temperature. Five-hundred microlitre pulses of 5% CO/Ar were introduced, and the CO uptake profile was measured using a TCD detector. The dispersion of Ru was calculated assuming a CO:Ru stoichiometry of 5:1 [25,26].

3. Results and discussion

3.1. Catalyst characterisation

To understand the effects of oxidation and reduction treatments on the structure and physicochemical properties of Ru/SAC catalysts, the catalyst samples, including the original Ru/SAC, the oxidised Ru/SAC and the reduced Ru/SAC, were characterised by BET, TEM, CO-TPD, Raman, XRD, TPR, TG and XPS. To enable a clear discussion, both fresh and used catalysts were characterised, and the related results are displayed together. The used catalysts previously experienced the acetylene hydrochlorination reaction for 48 h under the conditions of 170 °C, a C_2H_2/HCl feed volume ratio of 1:1.1 and a GHSV (C_2H_2) of 180 h^{-1}.

3.1.1. BET results

The N_2 adsorption–desorption isotherms of all of the fresh catalysts exhibit similar type-I adsorption isotherms (Fig. S1a) due to the large number of micropores in SAC. The pore size distributions of these Ru-based catalysts indicate an approximate modal size near 0.5 nm (Fig. S1b). Table 1 lists the specific surface areas and total pore volumes of the fresh and used Ru-based catalysts. For the fresh catalysts, the specific surface area decreases in the order of Ru/SAC-C300 (1107 m²/g) > Ru/SAC-C200 (1089 m²/g) > Ru/SAC (954 m²/g) > Ru/SAC-R300 (922 m²/g) > Ru/SAC-R400 (882 m²/g) > Ru/SAC-R500 (867 m²/g) > Ru/SAC-C400 (766 m²/g), and the pore volume of these fresh catalysts displays a similar trend. This suggests that an oxidation treatment at 200–300 °C can increase the specific surface area and the pore volume of Ru/SAC catalysts; however, at a high oxidation temperature (400 °C), the pore structures of catalysts are destroyed to some extent, resulting in the lowest surface area and pore volume. In addition, the reduction treatment results in a decrease in the surface area, with higher reduction temperatures resulting in lower surface areas.

In the case of the used catalysts that have been assessed in the acetylene hydrochlorination reaction for 48 h, both the surface area and pore volume are lower than those of the corresponding fresh catalysts. The used Ru/SAC exhibited a decrease in the surface area and pore volume of 13 and 17%, respectively. The used Ru/SAC-C300 exhibited the lowest decrease in surface area (4%) and pore volume (10%), followed by the used Ru/SAC-C200 (6% decrease in surface area and 12% decrease in pore volume). The used Ru/SAC-C400 exhibited the highest decrease in surface area (20%) but a relatively small decrease in pore volume (7%). For the used Ru/SAC-R300, Ru/SAC-R400 and Ru/SAC-R500, the individual decreases in the surface area and pore volume were smaller than those of the