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Research paper

Improvement of imidazolium-based ionic liquids on the activity of ruthenium catalyst for acetylene hydrochlorination

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ABSTRACT

Imidazolium-based Ionic Liquids (IBILs) were employed to synthesize Ru-based catalysts using the Supported Ionic Liquid Phase (SILP) technique for acetylene (C_2H_2) hydrochlorination, combining the characterizations of transmission electron microscopy (TEM), N_2 adsorption-desorption (BET), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD), and X-ray photoelectron spectra (XPS), etc. The optimal Ru10%[BMIM]BF_4/AC catalyst achieved the C_2H_2 conversion of 98.9% and the selectivity to vinyl chloride monomer (VCM) of 99.8% under the temperature of 170 °C and the C_2H_2 gas hourly space velocity (GHSV) of 180 h^{-1}. Further, other IBILs with different anions were chosen to fabricate Ru-based catalysts, and the catalysts showed high activity and selectivity similar with Ru10%[BMIM]BF_4/AC catalyst. It is demonstrated that IBILs additives can significantly improve the dispersion of ruthenium species and prevent the appearance of coke deposition owing to the interactions between Ru species and [BMIM]BF_4. Moreover, the oxygen-containing functional groups on the carbon support are associated with the interactions among Ru species and [BMIM]BF_4.

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1. Introduction

Vinyl chloride, the important monomer to produce the popular plastic polyvinyl chloride (PVC), is industrially produced via the acetylene hydrochlorination reaction with the mercury chloride (HgCl$_2$) catalyst in coal-based economic countries [1,2]. The active component HgCl$_2$ is easily volatile at the reaction condition, leading to the deactivation of the catalyst [3,4] but also the severe hazards to the environment ecology and the human health. In October 2013, approximately 140 countries signed the Minamata Convention in Japan aiming at forbidding the application of mercury worldwide in near future [5,6]. Consequently, it is crucial to explore an efficient and non-mercury catalyst for the hydrochlorination of acetylene.

Au-based catalysts have been intensively studied as the non-mercury catalyst for acetylene hydrochlorination [7,8], in particular, bimetallic Au-based catalysts including the additive of the secondary metal of Cu [9,10], La [11], Ba [12], Cs [13], Bi [14], or Sn [15], etc., and the trimetallic Au-Co-Cu catalyst have showed much better catalytic activities [3]. However, in the view of industrial production, the promising non-mercury catalyst should possess the feature of high activity, long-term stability as well as low cost.

Ruthenium-based catalysts have recently attracted more attentions for acetylene hydrochlorination owing to the comparable catalytic activity but much lower cost of ruthenium, comparing with that of gold [16–23]. For instance, bimetallic catalyst 1%Ru1Co(III)3/SAC showed an C_2H_2 conversion of 95% at 170 °C and the C_2H_2 GHSV of 360 h^{-1} [16]. Trimetallic catalyst Ru1Co(III)3Cu(II)1/SAC showed an C_2H_2 conversion of 99.0% for at least 500 h at 170 °C and the C_2H_2 GHSV of 90 h^{-1} [23]. However, Ru-based catalysts face up with the challenge of coke deposition during long time reaction. For the catalyst Ru1Co(III)3Cu(II)1/SAC experienced 48 h reaction, the coke deposition amount is of 2.4%, while 1%Ru1Co(III)3/SAC catalyst after 24 h reaction possessed the coke deposition of 3.25%. Thus, it is fundamental to explore effective method to inhibit the coke deposition so as to enhance the stability of Ru-based catalysts.

In recent years, more attentions have been gravitated towards room temperature Ionic Liquids (ILs) attributed to the advantage of high thermal stability, superior solubility for a wide variety of organic, inorganic, and polymeric molecules [24]. With the aid of the Supported Ionic Liquid Phase (SILP) technique, ILs can form a thin film on the catalyst surfaces providing the homogeneous solvent environment, facilitating the mass transport, thus stabilizing the transition metal catalyst. For instance, the com-

mon Imidazolium-based Ionic Liquids (IBIL) with the melting temperatures below 100 °C have been applied in many reactions, such as hydrogenation [25], hydrogenation of benzene to cyclohexene [26], hydroformylation [27–29], hydroamination [30], hydroaminomethylation [31], and propylene epoxidation [24]. In 2012, He et al. studied the solubility of hydrogen chloride in three kinds of ILs, demonstrating that [BMIM]Cl has the outstanding dissolution towards HCl [32]. Zhao et al. investigated the solubility of acetylene in room-temperature ILs through the theoretical calculation, indicating that room-temperature ILs of [bmim][OAc] and [bmim][BF$_4$] have the superior solubility toward C$_2$H$_2$ [33]. Zhao et al. prepared the Au(III)–IL/AC catalyst using the Ionic Liquid (1-propyl-3-methylimidazolium chloride) and the precursor of HAuCl$_4$·4H$_2$O, which provided the C$_2$H$_2$ conversion of 77.1% under the conditions of 180 °C and the C$_2$H$_2$ GHSV of 370 h^{-1} [34]. These interesting results enlightened us to study whether or not Ru-based catalysts can be improved by suitable ILs for acetylene hydrochlorination.

In this article, we adopted Imidazolium-based Ionic Liquids (IBILs) to modify Ru-based catalysts using the Supported Ionic Liquid Phase (SILP) technique, and assessed the catalytic performance for C$_2$H$_2$ hydrochlorination. Characterized by TEM, TPD, N$_2$ adsorption-desorption, TGA and XPS, etc., the optimal IBIL was selected and the effect of IBIL additives on the catalytic activity of Ru-based catalysts were studied.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Chemicals

Coconut activated carbon (AC, 24–35 mesh) was used as the support purchased from Fujian Sensen Carbon Industry Science and Technology Company with limited liability. In addition, the commercial carbon was used directly without further purification. RuCl$_3$·3H$_2$O (Ru content ≥ 38%, purity ≥ 99%) was purchased from Tianjin Fengchuan Reagent Co. Ltd. and used as the precursor. 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$, purity ≥ 97%) and 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$, purity ≥ 97%) were purchased from Shanghai Shaoyuan Chemical Technology Co. Ltd. 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl, purity ≥ 99%) were purchased from Shanghai Demo medical Technology Co. Ltd. In this study, all chemicals were used without pre-treatment.

2.1.2. Pristine Ru/AC catalyst

RuCl$_3$·3H$_2$O was used as the precursor to prepare Ru-based catalysts by the incipient wetness impregnation method [19,22]. Activated carbon were added to the solution of RuCl$_3$·3H$_2$O in tri-distilled water at room temperature under stirring with the Ru loading of 1 wt%, followed by ultrasonic treatment for 10 min ensuring that the precursor was uniformly adsorbed on the surface of activated carbon. Next, the overall mixture was incubated at 60 °C keeping 12 h and was then desiccated at 150 °C keeping 12 h in the vacuum drying oven. The obtained catalyst was named as Ru/AC.

2.1.3. Ru-IBILs catalysts

Ruthenium [BMIM]BF$_4$ catalysts were prepared by adding the RuCl$_3$·3H$_2$O quantitatively into [BMIM]BF$_4$ as a precursor, then the mixture was dissolved in tri-distilled water under stirring, followed by ultrasonic treatment for 10 min. Supported Ru-[BMIM]BF$_4$ catalysts were synthesized by adding the AC to the Ru-[BMIM]BF$_4$ solution in certain ratio with fast stirring under room temperature, and then aging at 60 °C for 12 h. After, the products were dried at 150 °C in the vacuum drying oven for 12 h and denoted as Ru1%[BMIM]BF$_4$/AC, Ru5%[BMIM]BF$_4$/AC, Ru10%[BMIM]BF$_4$/AC

and Ru15%[BMIM]BF$_4$/AC with the Ru loading of 1 wt% and the various mass contents of [BMIM]BF$_4$ from 1 wt% to 15 wt%. Moreover, Ru-[BMIM]PF$_6$/AC and Ru-[BMIM]Cl/AC catalysts were prepared by the same procedure with the Ru loading of 1 wt% and the IBILs loading of 10 wt%.

2.2. Catalytic property tests

These catalysts were evaluated in a fixed bed stainless steel microreactor (internal diameter of 10 mm, the length of 50 cm). The temperature was controlled by a CKW1100 temperature controller purchased from Beijing Chao Yang Automation Instruments Factory. The clean C$_2$H$_2$ was first purged using silica-gel desiccant, and HCl gas was passed through molecular sieves to remove the trace water. Firstly, the whole system was purged by introducing N$_2$ continuously to remove air and water. Before reaction, the high-purity HCl gas (16.5 mL min^{-1}) was fed through the microreactor for 30 min at 170 °C. Then, C$_2$H$_2$ (15.0 mL min^{-1}) was introduced into the microreactor starting reaction at the condition of 170 °C and the C$_2$H$_2$ GHSV of 180 h^{-1}. The effluent stream was first passed into NaOH aqueous solution to remove the superfluous HCl gas, and then analyzed by Bei Fen 3420A gas chromatograph with a flame ionization detector (FID).

2.3. Catalyst characterization

TEM was performed on an FEI Titan 80300 TEM/STEM (FEI, USA) at the acceleration voltage of 200 kV. The catalyst powder was first dispersed in absolute ethyl alcohol and then centrifuged to get the supernatant.

BET pore structure and specific surface areas were measured using the Quantachrome Instruments autosorb analyzer (Quantanchrome, USA). The samples were degassed at 220 °C for 4 h, then analyzed using liquid nitrogen adsorption and desorption at 77 K.

TGA was carried out on TG-DTG simultaneous thermal analyzer (NETZSCH STA 449F3 Jupiter®, Germany) under air atmosphere with a flow rate of 20 mL min^{-1} or nitrogen atmosphere with a flow rate of 50 mL min^{-1} with a heating rate of 10 °C min^{-1} from 35 °C to 900 °C.

TPD was conducted by an AutoChem BET TPR/TPD (Quantachrome, USA) to investigate the adsorption and desorption property of catalysts for reactants and products. Firstly, 120 mg catalysts adsorbed C$_2$H$_2$ or HCl at 170 °C for 4 h in the microreactor individually. Then, the catalysts were transferred to TPD instrument and treated with pure He for 30 min, followed by desorbing in a rate of 10 °C min^{-1} from 50 to 700 °C. For the C$_2$H$_3$Cl-TPD, 120 mg catalysts were pre-treated with C$_2$H$_3$Cl for an hour at 170 °C on the TPD instrument, and then tested at the same conditions with reactants-TPD. CO-TPD was measured by this instrument, with the samples reduced at 400 °C for an hour in the atmosphere of H$_2$/Ar. The CO uptake profile was detected by a TCD detector, and the calculation of the ruthenium dispersion assumed the adsorption ratio for CO: Ru equaling 1:1.

X-ray photoelectron spectra were performed with a Thermo ESCALAB 250XI (Thermo Fisher Scientific, USA) using a monochromatic AlKα X-ray source. The binding energies were calibrated with the C1s level of carbon at 284.8 eV.

3. Results and discussion

3.1. Performance of Ru-[BMIM]BF$_4$/AC catalysts

Fig. 1 presents the performance of the supported Ru-[BMIM]BF$_4$ catalysts for the acetylene hydrochlorination reaction, together with that of the support AC and the IL-supported 10%[BMIM]BF$_4$/AC