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The influence of different precipitants on the copper-based catalysts for hydrogenation of ethyl acetate to ethanol

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ARTICLE INFO

Article history:

Received 8 March 2014
 Received in revised form
 6 May 2014
 Accepted 9 May 2014
 Available online 9 June 2014

Keywords:

Ethanol fuel
 Precipitant
 Hydrogenolysis
 Ethyl acetate
 Cu/ZnO/SiO₂

ABSTRACT

Ethanol fuel has become a hot topic in the economic, political, environmental, and scientific areas. In this work, a new way for the synthesis of ethanol by hydrogenolysis of ethyl acetate is introduced and the impact of different precipitants on the ethyl acetate hydrogenolysis catalysts is systematically investigated by several considerations, including dispersion effects, the texture of the catalysts, and the copper phases in the surface layer of the reduced catalysts, etc. These precursors and catalysts are characterized by inductively coupled plasma-atomic emission spectroscopy, N₂-adsorption, X-ray diffraction, transmission electronic microscope, H₂ temperature-programmed reduction and X-ray photoelectron spectroscopy. It is confirmed that the choice of precipitant is of great importance. The samples are classified into two types, depending on the anion of precipitant. Except the catalyst prepared by (NH₄)₂CO₃, in which low copper loading is observed, type B catalysts (–CO₃²⁻) possess smaller copper particles and larger BET surface than that of type A catalysts (–OH), while the difference of catalysts in the same type is not obvious. Moreover, the coexistence of Cu⁺ and Cu⁰ is only detected in reduced type B catalysts. In general, ethyl acetate hydrogenolysis activity varies considerably with the precipitant, in the following order: Na₂CO₃ ≥ NaHCO₃ > NaOH ≥ KOH > (NH₄)₂CO₃.

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Introduction

As a potential alternative to oil, ethanol fuel has become a hot topic in the economic, political, environmental, and scientific areas [1]. The synthesis of ethanol by hydrogenolysis of ethyl acetate is of great commercial potential, since ethyl acetate can be produced at lower cost and on a large scale.

The catalytic hydrogenolysis of esters to their corresponding alcohols [Eq. (1)] has been extensively studied since the first report by Flokers and Adkins [2].



A mechanism for acetate hydrogenolysis was proposed by Yan et al. [3] and Evans et al. [4] The acetate is adsorbed dissociatively [Eq. (2)]

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where * indicates a catalytic site on the surface. Isotopic labeling studies showed that the alkoxy fragment $\text{R}'\text{O}^*$ reacts quickly to form $\text{R}'\text{OH}$, while the acyl group RCO^* is adsorbed longer. Thus the hydrogenation of the acyl fragment is believed to be the rate-determining step during acetate hydrogenolysis. The acyl group can be hydrogenated either to the desired alcohol or to the corresponding aldehyde, which is subsequently hydrogenated [3,5]. An in situ infrared spectroscopy investigation [6] during ethyl acetate hydrogenolysis gained further evidence for the proposed mechanism via dissociatively adsorbed fragments. Furthermore, Kenvin and White [7] could explain their results based on the mechanism proposed by Evans et al.

For ester hydrogenolysis, copper-based catalysts including copper chromite, silica-supported copper and Raney copper are well known to exhibit high activities [5,8,9], and the experimental results strongly indicate that copper is the essential catalytic component in the ester hydrogenolysis reaction [8]. Moreover, the addition of metal oxides, such as Cr_2O_3 , ZrO_2 , Fe_2O_3 or ZnO , etc. has been extensively investigated to promote the activity of Cu in the hydrogenolysis reaction [10]. When both activity and selectivity were taken into account, Brands [9] and van de Scheur [11] concluded that ZnO was the promoter of choice. It has been reported [10,11] that the addition of ZnO into copper-based catalyst can lead to a higher Cu dispersion (i.e., a smaller Cu particle), and ZnO is believed to act as a structural promoter in enhancing the area of Cu, the active site for the reaction.

According to references [5,10,12–14], coprecipitation method is a conventional preparation method for ester hydrogenolysis catalysts, thus, the choice of precipitants is of great importance. Kim et al. [10] and Yuan et al. [12] chose NaHCO_3 and Na_2CO_3 as the precipitant in the references, respectively, while Chen et al. [14] reported that the Cu/SiO_2 catalysts precipitated by NaOH showed high activity in hydrogenation of ester. In general, the impact of different precipitants on the performance of ethyl acetate hydrogenolysis catalysts has never systematically investigated.

In this work, the silica supported Cu–Zn catalysts were prepared via coprecipitation method for hydrogenation of ethyl acetate, and the main aim of this study is to have a better view of the influence of different precipitants on the catalysts by several considerations, including dispersion effects, metal loading, the texture of the catalysts, and the copper phases in the surface layer of the reduced catalysts, etc. The characterization results are discussed alongside with the catalytic data obtained using a laboratory fixed-bed reactor.

Experimental

Catalyst preparation

Hydrogenation components Cu–Zn/ SiO_2 (Cu/Zn/ SiO_2 molar ratio = 2:1:1) were prepared by coprecipitation method. In a round bottom flask, appropriate amount of silica sol (Sinopharm Chemical Reagent Co., Ltd., China, 30%) was mixed with distilled water under vigorous stirring. Required

amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., China, AR) were dissolved in 200 ml distilled water at room temperature, and this solution was referred as A, in which $\text{Cu}^{2+}/\text{Zn}^{2+} = 2$ and $\text{Cu}^{2+} + \text{Zn}^{2+} = 0.5 \text{ mol/L}$. Solution B (200 ml) was an aqueous of the precipitant [NaOH , KOH , Na_2CO_3 , NaHCO_3 or $(\text{NH}_4)_2\text{CO}_3$ (Sinopharm Chemical Reagent Co., Ltd., China, AR)]. Then solution A and solution B were simultaneously added dropwise (in around 1 h) to the round bottom flask with vigorously stirring in the ambient temperature, the pH was maintained at 8.0 during dripping process by controlling the flow velocity of solution A and solution B.

After completing the process of precipitation, the resulted suspension was stirred for 30 min, filtered and washed five times with distilled water until the pH of filtrate reached 7.0. The precipitate was dried in an oven at 120°C overnight and then calcined in a muffle furnace in air by heating at 500°C for 5 h. Finally, the resulting catalysts were crushed and sieved. The 20–40 mesh particles were used for the activity test.

The prepared catalysts were labeled as $\text{Cu}_2\text{Zn}_1\text{Si}_1\text{-M}$, where M stands for the precipitant used in the process of catalysts preparation. Herein, the samples are classified into two types, depending on the anion of precipitant. The $\text{Cu}_2\text{Zn}_1\text{Si}_1\text{-NaOH}$ catalyst and $\text{Cu}_2\text{Zn}_1\text{Si}_1\text{-KOH}$ catalyst are referred as type A, and the other three are referred as type B.

Characterization of catalyst

Inductively coupled plasma-atomic emission spectroscopy

Actual metal loading in the calcined catalysts was determined with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a multichannel Thermo Jarrel-Ash ICP 612 E spectrometer.

N_2 -adsorption

Nitrogen isotherms were measured at -196°C with an ASAP 2020 (Micromeritics). Before experiment, the samples were heated at 120°C and outgassed overnight at this temperature under a vacuum of 10^{-5} Torr to a constant pressure. N_2 isotherms were obtained in both adsorption and desorption modes. The surface areas of the calcined catalysts were determined by the BET method. The total pore volume (TPV) was calculated from the amount of vapor adsorbed at a relative pressure (p/p_0) close to unity (desorption curve), where p and p_0 are the measured and equilibrium pressures, respectively. Pore size distribution curves were established from the desorption branches of the isotherms using the BJH model [15].

X-ray diffraction

X-ray diffraction (XRD) technique was used to characterize the crystal structure. The experiments were performed using a Siemens D500 diffractometer, using $\text{Cu K}\alpha$ radiation (40 kV, 100 mA) and equipped with a graphite monochromator with a reflected beam. The powder diffraction patterns were recorded in the 2θ range from 20° to 80° . An X-ray chamber-reactor was used for the high-temperature registration of the spectra.

Temperature-programmed reduction

Temperature programmed reduction (TPR) of H_2 was carried out on Auto Chem2910 (Micromeritics) instrument to study

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