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The selective hydrogenation of ethyl stearate to stearyl alcohol over Cu/Fe bimetallic catalysts

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ABSTRACT

Bimetallic and monometallic catalysts including Cu and/or Fe species were prepared by a co-precipitation method and their catalytic performance was tested for the selective hydrogenation of ethyl stearate to stearyl alcohol. The bimetallic catalysts were observed to be even more active for this selective hydrogenation compared to the monometallic catalysts and their physical mixtures. With a bimetallic catalyst of Cu/Fe (4/1 in mole ratio) reduced at 200 °C, a selectivity to the alcohol reached to above 99% at a conversion of 97% in reaction for 4 h at 230 °C, 3.0 MPa. Effects of composition and reduction temperature on the catalytic performance were studied and the properties of catalysts prepared under different conditions were examined by XRD, TPR, N_2 physisorption, and SEM. The relationship of the performance with the properties of the catalysts was discussed, along with the conditions under which synergistic effects of Cu and Fe species appeared and caused the enhancement of the catalytic performance.

1. Introduction

Fatty alcohols and their derivatives, especially higher alcohols, are industrially important intermediates in the synthesis of surfactants and plasticizers [1,2]. Higher alcohols are long chain fatty alcohols with a carbon number of 12–22, such as lauryl alcohol, cetyl alcohol and stearyl alcohol. The most commonly used method to produce fatty alcohols is the selective hydrogenation of fatty acids or fatty acid esters over heterogeneous catalysts [3,4]. Copper catalyst is a good candidate for the selective hydrogenation of C=O bond to alcohol without further hydrogenolysis of C—O bond formed [5,6]. Considering that copper itself is low active for this reaction, one should use supports or promoters to improve the activity and selectivity. Currently, copper catalysts, such as Cu/SiO_2, Cu/ZnO, $Cu–Zn/Al_2O_3$, have been widely studied for the selective hydrogenation of fatty esters to corresponding alcohols [7–9]. The influence of dispersion of Cu particles and the activation of hydrogen molecule and fatty esters are of importance [10–12]. Recently, it was reported that iron could act as an electronic/chemical promoter to modify metal catalysts and improve their catalytic activity and selectivity because it increased surface area and dispersion of host metal elements [13–15]. For example, the electronegative metal of Fe could enhance the selectivity of hydrogenation of unsaturated aldehydes to unsaturated alcohols over Pt catalyst [16,17]. An Fe modified CoB amorphous alloy catalyst increased the selectivity to crotyl alcohol during the selective hydrogenation of crotonaldehyde [18]. Therefore, the Fe modified catalysts may produce preferential adsorption sites for the C=O bond, thus enhancing the selective hydrogenation of C=O to C—OH. This would be due to the changes in structural and/or electronic properties of Cu species caused by the addition of Fe.

In this work, we prepared two kinds of Cu/Fe bimetallic catalysts by co-precipitation method and their catalytic performances were discussed for the hydrogenation of ethyl stearate to stearyl alcohol as a model reaction. The composition of Cu/Fe catalysts was found to greatly influence their catalytic behavior. The correlation of their catalytic performance with the properties of Cu/Fe catalysts, such as phase composition, morphology, specific surface area, pore diameter, and pore volume was discussed in detail. Strong electronic interactions of Cu and Cu_2O with Fe_3O_4 and Lewis acid sites should play crucial roles for high yield of fatty alcohol

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observed in the selective hydrogenation of ethyl stearate to stearyl alcohol.

2. Experimental

2.1. Synthesis and characterization of catalysts

All chemicals used in the present work are analytical grade and used without further purification. The Cu/Fe catalysts were prepared by a simple co-precipitation method. Typically, an aqueous solution of cupric nitrate ($Cu(NO_3)_3 \cdot 3H_2O$, 0.25 M) was mixed with an aqueous solution of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 0.25 M) with a Cu/Fe molar ratio of either 1/4 or 4/1. After the mixture solution was stirred at 80 °C for 30 min, an aqueous solution of sodium hydroxide (NaOH, 1 M) was added dropwise to the salt solution under vigorously stirring until the pH reached to ca. 9–10. The mixture obtained was further stirred at 80 °C for 4 h and then aged for another 1 h at room temperature. The precipitate formed was filtrated, washed with distilled water for several times to remove the impurities, and then dried at 110 °C. The samples so prepared will be denoted as Cu/4Fe-pre and 4Cu/Fe-pre in which Cu/Fe ratio is 1/4 and 4/1, respectively. These samples were calcined at 300 °C for 4 h in air; the samples will be denoted as Cu/4Fe-C300 and 4Cu/Fe-C300, respectively. For comparison, monometallic oxide materials were also prepared by similar procedures. The samples prepared before and after the calcination will be denoted as Cu-pre (Fe-pre) and Cu-C300 (Fe-C300), respectively. The samples were further reduced in hydrogen atmosphere at different temperatures (150, 200 and 500 °C) for 90 min, which will be denoted, for example, as Cu/4Fe-R150.

The structure and crystal phase composition of the samples were determined by powder X-ray diffraction patterns with a Brucker D8 GADDS diffractometer using Co K radiation (1.79 Å) and the crystallite size was calculated with the Scherrer's equation. The samples for XRD examination were reduced at a certain temperature and reserved in ethanol for avoiding exposure to air before XRD tests. The temperature-programmed reduction (TPR) analysis was performed under a flow of 5% H_2/N_2 mixture (30 ml/min), with a heating rate of 10 K/min. Surface acidity was studied by NH_3 temperature-programmed desorption (TPD) on a TP-5080 Multi-functional Automatic Adsorption Instrument (Tianjin Xianquan Industry and Trade Development Co. Ltd, China) equipped with a TCD. Prior to the TPD experiments, 100 mg of the catalyst sample was pre-reduced in situ at 200 °C for 90 min in a N_2/H_2 gaseous mixture. The morphology of the samples was recorded by scanning electron microscope (SEM Hitachi S-4800). N_2 adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020 Analzer (USA). The surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. Pore volume (V_p) was estimated using the adsorption branch of the N_2 isotherm curve. Pore size distribution curves were calculated by the Barrett–Joyner–Halenda (BJH) method using adsorption branch of the N_2 isotherms.

2.2. Activity test

Reaction experiments were carried out in a 50 ml stainless steel autoclave. All the catalysts were pre-reduced in hydrogen at temperature (150, 200, 500 °C) for 90 min before the reaction. After reduction, the catalyst was transferred into the autoclave, in which 5.0 ml hexane was added as solvent, under the protection of hydrogen. After that, a certain amount of ethyl stearate was added and the autoclave was sealed. The reaction was operated under a stirring rate of 1300 rpm (without diffusion limitation) at 230 °C and a H_2 pressure of 3.0 MPa H_2. After the reaction for several hours, the autoclave was cooled to room temperature. The products were collected and then analyzed by gas chromatography with FID detector with a DB-1 capillary column and GC–MS.

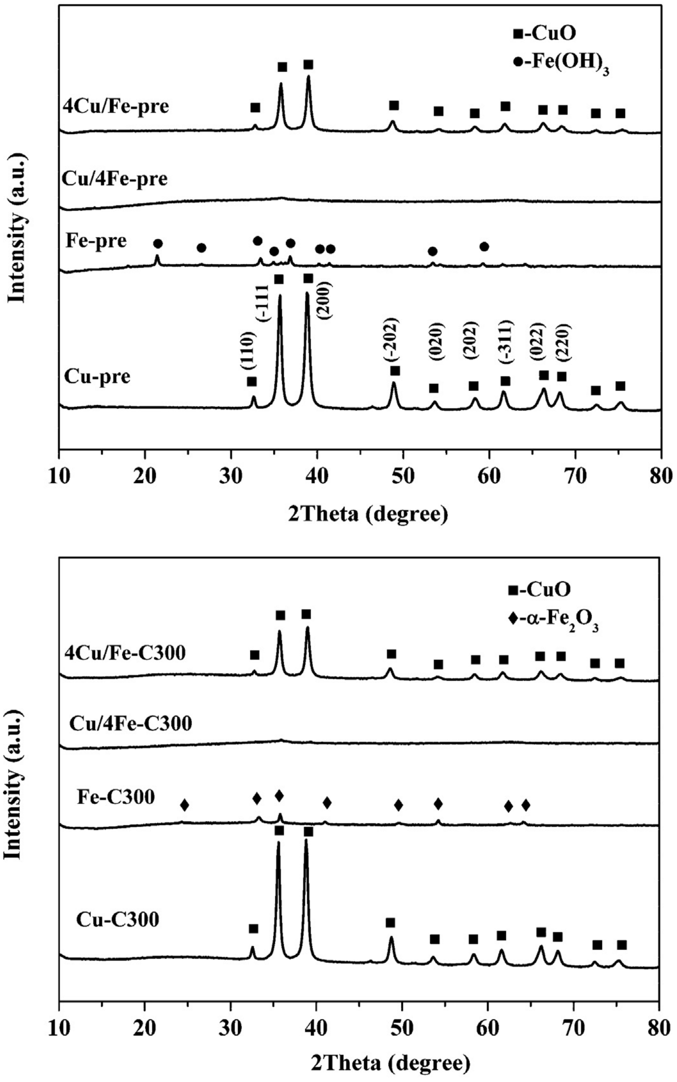

Fig. 1. XRD patterns of precursor and calcined samples.

3. Results and discussion

3.1. Textual properties and surface acidity

Fig. 1 shows the XRD patterns of the precursor and calcined Cu/Fe catalysts. The monometallic oxides, iron and copper oxides, were also analyzed for comparison. The Fe-pre sample gave a relative weak characteristic diffraction of $Fe(OH)_3$ (JSCPDS 29-0713), and after calcination at 300 °C it was transferred to α-Fe_2O_3 (JCPDS 33-0664). Both Cu-pre and Cu-C300 sample presented CuO phase. This is because that copper hydroxide $Cu(OH)_2$ was metastable and thermodynamically easy to transfer into more stable compound of CuO [19]. In this system, the aging temperature was 80 °C so that the precipitate $Cu(OH)_2$ formed was directly decomposed to CuO in the hot alkali solution [20]. For Cu/4Fe samples, no any diffraction peaks could be detected before and after the calcination at 300 °C, indicating that both the Cu and Fe existed in an amorphous state. Zhang et al. reported that a certain amount of Cu could prevent the crystallization of α-Fe_2O_3, and more importantly it could increase the temperature of phase transformation from $Fe(OH)_x$