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ScienceDirect

Catalysis Communications 9 (2008) 1201–1208

CATALYSIS COMMUNICATIONS

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Study of CuCoZnAl oxide as catalyst for the hydrogen production from ethanol reforming

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Received 27 June 2007; received in revised form 9 October 2007; accepted 5 November 2007
Available online 23 November 2007

Abstract

Ethanol steam reforming was studied over CuCoZnAl oxide with the addition of potassium. The catalyst was prepared by the coprecipitation method and characterized by X-ray diffraction, thermogravimetry, Raman spectroscopy, temperature programmed reduction, BET specific surface area and SEM-EDAX. The influence of reaction temperature was examined between 400 and 600 °C with a H_2O/C_2H_5OH molar ratio of 3.8. At 600 °C, the catalyst was very active with an ethanol conversion of 100%. The main products were CO_2 and CO and minor amounts of CH_4. The hydrogen yield was 5.2 mol of H_2 per mol of ethanol, which means a high hydrogen selectivity (87%). Stable activity and selectivity were obtained at 600 °C which could be attributed to the removing of carbonaceous deposits.

Keywords: Ethanol reforming; Hydrogen production; Mixed oxide catalyst

1. Introduction

In recent years, as a consequence of the foreseen reduction in fossil resources and environmental constraints, a great interest for new energy sources has been shown. The hydrogen has been pointed out as the alternative fuel, and the scientific community has oriented a lot of research works to the generation, storage and transportation of hydrogen. Different raw material and reactions have been proposed to the hydrogen production. In this sense, ethanol from biomass has a great potential not only because the renewable origin but also for its rich hydrogen content. According to the ethanol steam reforming reaction

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 3CO_2$$

a maximum yield of six moles of hydrogen for each mol of ethanol could be obtained. However, many side reactions leading to the production of rich hydrogen compounds like CH_4, C_2H_4O, C_3H_6O, C_2, C_3 reduce the expected hydrogen yield. Besides, some of these compounds act as coke precursors leading to the formation of carbonaceous deposits. The development of an active, highly selective and very stable catalyst has become one of the keys in the hydrogen production. Different catalytic systems based on Cu, Co, Ni, Cu–Ni and Cu–Co oxides, with and without alkaline addition, [1–13] have shown to be active for ethanol reforming with variables hydrogen selectivities. The support seems to play an important role in the steam reforming reaction: (i) it should favour water splitting into OH groups and promote their migration to the metal particles; (ii) it should promote the dehydrogenation route for decreasing the deactivation by coke; and (iii) it should contribute to the stabilization of the metal particles at high temperature under steam [14]. Aluminium spinels seem to be a good option as catalytic supports. They are stable

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doi:10.1016/j.catcom.2007.11.015

under reforming conditions, mechanically resistant and present a low surface acidity [15]. When ternary Cu/Co(Zn)/Al oxides were prepared by coprecipitation method the formation of spinels was detected [16–18]. As far as we known the catalytic system CuCoZnAl has not been examined in the ethanol steam reforming. In this work the results of the synthesis, characterization, activity and stability of a CuCoZnAl catalyst modified by the K are reported.

2. Experimental

The catalyst was prepared by coprecipitation method from an aqueous solution of the metal nitrates with K_2CO_3 at 60 °C and pH = 7 in a stirred batch reactor [18]. After precipitation, the solid was collected by filtering and washed with hot (90 °C) distilled and deionzed water (400 ml). This washing step was carried out in order to partially remove K content. Then, the solid was dried overnight at 70 °C and finally underwent a decomposition process at a final temperature of 500 °C for 480 min. The decomposition was carried out under N_2 flow (30 ml min^{-1}) by using a temperature program which was determined from TGA experiment of the precursor. The Cu and Co nominal loading was fixed to 12 wt.% and the molar ratio Zn:Al = 0.5. The chemical composition of catalyst was confirmed by atomic absorption spectroscopy.

The BET surface area was measured by using a Micromeritics Accusorb 2100E instrument by adsorption of nitrogen at −196 °C. XR diffraction patterns (XRD) were obtained with a RIGAKU diffractometer operated at 30 kV and 20 mA by using Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm) at a rate of 3 °C min^{-1} from $2\theta = 10°$ to 80°. The TG analyses were recorded by using TGA 51 Shimadzu equipment. The sample was heated from room temperature to 1000 °C at 10 °C min^{-1} with a N_2 (or air) flow of 50 ml min^{-1}. Scanning electron micrographs were obtained in a LEO 1450 VP. This instrument is equipped with an energy dispersive X-ray microanalyzer, EDAX Genesis 2000 with Si(Li) detector, which permitted analytical electron microscopy measurements. The samples were sputter coated with gold. The Raman spectra were run with a JASCO TRS-600SZ-P equipped with a CCD detector. The samples were excited with the 514 nm Ar line and the spectra acquisition consisted of five accumulations of 180 s for each sample. The reducibility was studied by hydrogen temperature programmed reduction (TPR) in a conventional equipment. The sample was pretreated in He at 300 °C for 60 min, cooled at 25 °C and reduced a 30 ml min^{-1} flow of 5 vol% H_2 in N_2, from 25 to 700 °C at a rate of 5 °C min^{-1}, and held at 700 °C for 2 h. Hydrogen consumption was monitored by a thermal conductivity detector after removing the water formed.

The ethanol steam reforming reaction was carried out in a fixed-bed quartz tubular reactor operated at atmospheric pressure. The reaction temperature was measured with a coaxial thermocouple. The feed was a gas mixture of ethanol, water and helium. Ethanol and water were fed through independent saturators before mixing. The flow rate was 70 ml min^{-1} at room temperature with an ethanol molar composition of 3%. The $H_2O:C_2H_5OH$ molar ratio was 3.8 in all the experiments. The catalyst weight was 300 mg (0.3–0.4 mm particle size). The catalyst was heated to the reaction temperature under He flow, then the mixture with $C_2H_5OH + H_2O$ was allowed to enter into the reactor to carry out the catalytic test. In all the cases fresh samples were used. The reactants and reaction products were analyzed on-line by gas chromatography. H_2, CH_4, CO_2 and H_2O were separated by a 1.8 m Carbosphere (80–100 mesh) column and analyzed by TC detector. Nitrogen was used as an internal standard. Besides, CO was analyzed by a flame ionization detector after passing through a methanizer. Higher hydrocarbons and oxygenated products (C_2H_4O, C_2H_4, C_3H_6O, C_2H_5OH, etc) were separated in RT-U PLOT capillary column and analyzed with FID using N_2 as carrier gas. The homogeneous contribution was tested with the empty reactor. These runs showed no activity at 500 °C whereas the ethanol conversion was 3% at 600 °C being acetaldehyde the only product.

Ethanol conversion, selectivity to products and yield to hydrogen were defined as

$$X_{\mathrm{EtOH}} = \frac{F^{\mathrm{in}}_{\mathrm{EtOH}} - F^{\mathrm{out}}_{\mathrm{EtOH}}}{F^{\mathrm{in}}_{\mathrm{EtOH}}} 100$$

$$S_i = \frac{v_i F^{\mathrm{out}}_i}{2(F^{\mathrm{in}}_{\mathrm{EtOH}} - F^{\mathrm{out}}_{\mathrm{EtOH}})} 100$$

$$Y_{\mathrm{H2}} = \frac{F^{\mathrm{out}}_{\mathrm{H2}}}{F^{\mathrm{in}}_{\mathrm{EtOH}}}$$

Being F^{in}_i and F^{out}_i the molar flow rates of product "i" at the inlet and outlet of the reactor and v_i the number of carbon atoms in "i".

3. Results and discussion

Table 1 summarizes some characteristics of the catalyst. It can be observed that the achieved compositions are in good agreement with nominal ones. XRD patterns are shown in Fig. 1. The precursor shows a crystalline hydrotalcite phase, Fig. 1a, which is completely decomposed after the thermal treatment. The diffraction pattern of final solid after decomposition reveals broad peaks at values of 2θ which could be corresponded to different spinel phases: $ZnAl_2O_4$, $CoAl_2O_4$, Co_3O_4, Fig. 1b. Complementary studies (shown forward) indicate that those peaks mainly corre-

Table 1
Chemical composition and specific surface area of CuCoZnAl catalyst after N_2 decomposition

	Co	Cu	Zn	Al	S_{BET} ($m^2\,g^{-1}$)
Nominal composition (wt.%)	11.3	12.2	25.1	20.7	34
Actual content (wt.%)	9.8	13.8	n.d.	20.1	