Hydrogen Production by Ethanol Steam Reforming over Co-Hydrotalcites

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Introduction

Many catalysts have been studied to produce H_2 from ethanol using metals such as Rh,Pt,Ni,Co,Zn,Fe,Cu,Au,Pd and Ru with diverse supports of metallic oxides as Al_2O_3[1], CeO_2[2], MgO[3], ZnO[4], SiO_2, Sm_2O_3, TiO_2,V_2O_5 [5] La_2O_3, Y_2O_3[6] ZrO_2[7]. From many investigations, we can deduce that the activity and the distribution of products depended on the type and concentration of metal, of the type of support and the preparation method. The biggest interest is to find active catalysts that inhibit the coke formation and especially of the CO that is harmful for the Fuel Cells. The hydrotalcites are not commonly used for the production of H_2 however they have basic sites which are important to prevent the formation of CH_2=CH_2 from ethanol. We have shown that for these catalysts the Co promoted the selectivity of ethanol to H_2 (71%) at 100% of conversion with 10wt%Co [8], Co promoted the thermal stability and produced low amounts of CO (< 1.2 %).

Materials and Methods

The hydrotalcites were prepared by the coprecipitation method with aqueous solutions of $Mg(NO_3)_2$, $Al(NO_3)_3$ and $Co(NO_3)_2$ (Aldrich) over a basic solution of Na_2CO_3 and NaOH (pH=10) having a atomic ratio of Mg/Al of 2/1.The Co metal changed from 0,2.5,5 and 10wt%Co. After the precipitation the samples were filtered, washed and dried at 120°C for 10 h.The samples were characterized by N_2 physisorption (BET area),Thermal gravimetric analysis(TGA) and Differential thermal analysis (DTA).Temperature Programmed Desorption (TPD) of CO_2, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and finally the ethanol steam reforming reaction. The reaction tests were made under differential reactor conditions. A constant mixture of N_2 and H_2O/CH_3CHOH =4 (molar ratio) was supplied to the reactor at 92°C. The reaction temperature was increased from 500 to 650°C and the products were analyzed by two gas chromatographs (Varian 3380 and Gow-Mac 550) using flame ionization and thermal conductivity detectors.

Results and Discussion

Two basic sites located at 230 and 335°C were found from TPD of CO_2. Different species on the surface reveled that the content of oxygen of different nature such as unidentate, bidentate and bicarbonate species formation involving surface hydroxyl groups. High surface areas were obtained (Table 1).The particles observed by SEM showed porosity and made of layers with a lamellar structure with 6 µm between layers. From XRD symmetrical reflections and broad asymmetric peaks were characteristic of the materials with laminar structure. These catalysts produced high ethanol steam conversions (near 100%), high selectivity to hydrogen (71%) and low selectivity to CO (Figure 1) from 500 to 650°C. The catalyst with 10wt%Co showed the best selectivity to H_2 with 100% of conversion at 500°C

Table 1. Surface area and Basic sites by TPD of CO_2 for Co-hydrotalcites.

Catalyst	Co (wt%)	Area BET (m^2/g)	Basic sites at 230°C (basic sites/g cat.)	Basic sites at 335°C (basic sites/g cat.)	Total basicity (basic sites/m^2)
MH	0	275	6.8×10^{21}	0	2.50×10^{19}
MH2.5	2.5	274	6.9×10^{21}	0	2.51×10^{19}
MH5	5	219	0.9×10^{21}	4.20×10^{21}	2.32×10^{19}
MH10	10	184	1.45×10^{21}	4.45×10^{21}	3.20×10^{19}

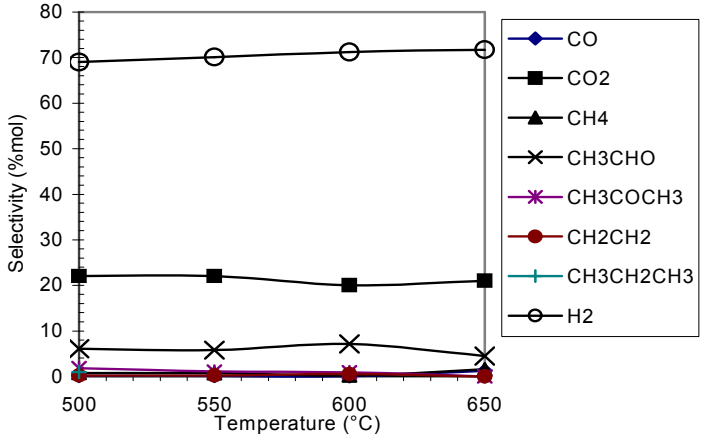

Figure 1.Effect of reaction temperature in the H2 production by ethanol steam reforming over a 10wt%Co-Hydrotalcite

Significance

For this Co-Hydrotalcite catalysts, a direct relationship between the Co concentration, the conversion and the total basicity was found and it is the first catalyst using a hydrotalcite reported in ethanol steam reforming to produce H_2.

References

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