Effect of metal oxides concentration over supported cordierite monoliths on the partial oxidation of ethanol

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ABSTRACT

The effect of metal oxide concentration supported over monoliths was studied on the partial oxidation of ethanol. Nano-structured Co_3O_4, NiO and CuO oxide catalysts were prepared by means of polymerization–combustion technique using citric acid as chelating agent and washcoated over cordierite monoliths, which after combustion process were calcined and tested under isothermal conditions. X-ray diffraction (XRD) and high resolution transmission electronic microscopy (TEM) showed nanostructure and stable crystallite materials. These metal oxides were tested in the partial oxidation reaction, showing that metal oxide concentration influences the product distribution and selectivity. The maximum concentration for all samples was 12% of corresponding metal oxide (MeO), resulting in high conversions and H_2 selectivity. Diffuse reflectance infrared Fourier transform spectroscopy of adsorbed ethanol (DRIFTS-EtOH) and TPD desorption of ethanol showed the formation of intermediate ethoxy-species and preferential dehydrogenation reaction.

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1. Introduction

Hydrogen production from bio-ethanol by steam reforming (SRE) and partial oxidation of ethanol (POE) are gaining increasing attention and may become important industrial process [1,2]. Ethanol has several advantages compared to other raw materials, but the most important is its renewable nature and subsequent overall reduction in CO_2 emission. An additional benefit of POE is related with the fact that process can be ran under autothermal conditions, thereby is possible to eliminate the need for external heat. Moreover, is much faster than catalytic steam reforming, allowing a quick start-up and short response times [3].

Generation of hydrogen from ethanol via catalytic partial oxidation has been studied under several temperature ranges from 450 to 900 °C using catalytic systems based on noble metals and rarely based on nickel or cobalt. Although supported noble metal catalysts have shown high activity and stability [4–6], supported nickel and cobalt catalysts are available at much lower cost. Currently, the most important task in POE research is identification of economic and stable catalysts.

Ethanol partial oxidation follows a very complex pathway, including several reaction intermediates formed and decomposed on both, supports and active metals comprising the catalytic systems. The nature of the support and the metal directly influences product distribution and catalyst stability during ethanol conversion reactions [7,8]. Several active phases have been proposed to serve as catalyst for this reaction [9,10].

Catalyst efficiency is one of the most important aspects in partial oxidation of ethanol (POE), since it is directly related with concentration of active catalytic phase. The use of transition metal oxides have been investigated by several authors and among the most important catalyst Co, Ni and Cu oxides representing the most active, selective and low cost materials for eventual applications. Recently the literature [11] reported the behavior of different catalysts for the partial oxidation of ethanol (POE), suggesting the promotion of dehydrogenation and dehydration reactions.

The use of different metal oxides concentration supported on alumina, indicates that high concentrations did not affect the activity and selectivity [12–16]. There are several publications reported in the literature related to the hydrogen production from ethanol, using nickel, cobalt, copper, chrome, noble metals and other catalytic metallic oxides as powders, pellets and ceramic foams, fed with water/ethanol mixtures with the main objective to identify some important catalytic aspects for the hydrogen production and high added-value products [13–20]. The partial oxidation of ethanol was studied under isothermal conditions based on previous thermodynamic predictions [21–23].

Based on these facts, we focus our investigation on systems derived from Co, Ni and Cu oxides, varying the metal oxide

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concentration supported over γ-Al$_2$O$_3$/cordierite monoliths for the partial oxidation of ethanol, and the relationship between the physicochemical and catalytic properties. Additionally, study the effect of synthesis, using citric acid to form metal–organic complexes that seems to be an effective way to obtain active and selective materials for this reaction with satisfactory stability, carbon resistance and anti-sintering properties in comparison with traditional catalyst prepared by the solid state technique. Finally, we study the influence of the metal oxide concentration on the activity and selectivity of unreduced metal oxides and the stability for the partial oxidation of ethanol reaction under isothermal conditions at low and high temperatures.

2. Experimental

2.1. Preparation of catalysts

The honeycomb cordierite monoliths have a cell density of 400 cells in-2 (D = 12 mm, L = 8 mm). The catalyst was prepared by washcoating of different metal oxides over γ-alumina. The γ-alumina support was prepared with a transition alumina solution using methods described elsewhere [24] and dipcoated over monoliths as described previously [25–27].

The active phases of Co$_3$O$_4$, NiO and CuO were prepared by polymerization–combustion technique, starting from the corresponding nitrates Co(NO$_3$)$_2$·6H$_2$O (99.9%), Ni(NO$_3$)$_2$·6H$_2$O (99.9%) and Cu(NO$_3$)$_2$·9H$_2$O (99.99%), using citric acid monohydrated (99.99%). Stoichiometric quantities of each solid salt (0.01 mol) were added to 20 mL of absolute ethanol in different glass vessels, equipped with magnetic stirring (150 rpm), reflux system and temperature control, as described elsewhere [20]. Once reached complete dissolution of each precursor, citric acid was added at 0.5:1 molar ratio with respect to the total concentration of metal cation in dissolution. Several solutions of 0.5 molar concentrations were kept under reflux at 120 °C for 12 h, until formation of a viscous liquid, which was then impregnated on cordierite honeycombs for each case. After washcoating the monoliths were heated at 150 °C under air flux in an oven until complete solvent evaporation and calcined at 500 °C under oxygen flow for 4 h to eliminate carbonaceous residues. The excess was removed using an ultrasonic cleaner after completing several deposition cycles with 3, 12 and 25 (%, w/w), respectively, as reported previously [24]. These samples were kept in a chamber under controlled humidity (20%) before catalytic testing. The stoichiometric composition was calculated based on the total oxidizing and reducing valences (N/C), assuming total combustion of citrate species.

$$(NO_3)^- + C_6H_{18}O_7 \rightarrow 6CO_2 + N_2 + 9H_2O + \text{oxides} \qquad (1)$$
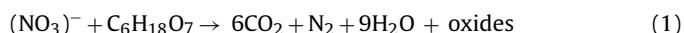
2.2. Characterization of catalysts

The chemical composition was obtained by X-ray fluorescence (XRF) technique, using an apparatus Rigaku Model RIX 3100. Samples were pressed as pellets and analyzed quantitatively. The specific area BET was evaluated by nitrogen adsorption isotherms at −196 °C, using an ASAP-2020 apparatus (Micromeritics). All samples were degassed at 350 °C overnight to remove residual humidity.

The crystalline structure was determined by X-ray diffraction, in a Miniflex Rigaku diffractometer, using Cu K$_\alpha$ radiation (λ = 1.54186 Å) between 10° and 90°, with steps of 0.05° and a speed analysis 0.15° min^{-1}. Refinement, indexing and the simulation of the structures were done with MAUD software that allowed establishing the chemical composition and crystallographic structure of the oxides. The crystallite sizes were calculated using the highest diffraction signals, using the Debye–Scherrer equation, taking the value of half peak width set by a Lorentzian function and using a constant of 0.89 as reference.

Temperature programmed reduction (TPR-H$_2$) was performed in a Micromeritics Pulse Chemisorb model 2705 equipment. The sample was heated at 200 °C for 2 h, flowing pure helium and then reduced with a mixture of 5% H$_2$/He (30 mL min^{-1}), rising up to the maximum temperature reduction at 10 °C min^{-1}. The H$_2$ consumption was measured using a thermal conductivity detector.

Scanning electron microscopy analysis (SEM) was performed using a LEO 440 microscope (Leica, Zeiss), equipped with an electron gun and a spectrometer measuring the energy dispersive X-ray. Images were obtained with a focus distance of 10–25 mm, an accelerating voltage of 20 kV and a current of 100–200 pA, measurement time of 100 s and count rate of 1.2 kcps. The samples were placed on a graphite holder bonded to a carrier of aluminum and shadowed with platinum to obtain a better contrast in the images.

Transmission electronic microscopy analysis (TEM) was performed on a JEOL 2100 equipment using a LaB$_6$ thermionic gun operated with an acceleration voltage of 200 kV, equipped with a CCD imaging system. For analysis, these samples were ground to obtain fine powders, which were sieved to 200 U.S. standard mesh and dispersed in a test tube with 5.0 mL of water and each tube was placed in a ultrasonic equipment for a period of 30 min, after which a drop of the top of each tube was taken and dried at 45 °C for respective analysis.

Diffuse reflectance infrared Fourier transform spectroscopy of ethanol adsorption (DRIFTS-EtOH) was carried out on a Nicolet spectrometer (Nexus 470 model), with a MCT detector and equipped with a diffuse reflectance chamber (Spectra Tech) for high temperature treatment. The *in situ* treatment was carried out using a feed composition of C$_2$H$_5$OH + O$_2$ (1:0.5 mL min^{-1}), which was analyzed at different temperatures (100, 200, 300 and 400 °C), using different residence times and collecting 150 spectrums per point.

Volumetric CO and H$_2$ chemisorption was performed in the ASAP-2020 Micromeritics equipment, using the volumetric technique. All samples were pretreated before adsorption and reduced at 500 °C for 1 h, under H$_2$ flow (50 mL min^{-1}). After reduction, sampler was evacuated for 1 h at 400 °C and cooled down at adsorption temperature under vacuum. Irreversible uptakes were determined from dual isotherms measurements for hydrogen at 150 °C and carbon monoxide at room temperature, according to the methodology described elsewhere [28]. To evaluate the metal surface, we used the following expression:

$$S_m = \frac{N_s}{[L]} \qquad (2)$$

where $[L]$ is the maximum density of sites or the number of surface metal atoms per m^2 and N_s is the number of surface sites, or the number of chemically adsorbed molecules. Considering the level of metal:

$$S_m = \frac{N_s}{y[L]} \qquad (3)$$

For calculation of dispersion percentage, we used the expression:

$$D(\%) = \frac{N_s}{N_t} \cdot 100 \qquad (4)$$

where N_t is the total number of atoms given by following expression:

$$N_t = \frac{y m_{cat}}{M} \cdot N_A \qquad (5)$$

where N_A is Avogadro's number, y the fraction of supported metal, m_{cat} is the mass of catalyst and M is the atomic weight of metal.