

Synthesis and characterization of Ni-Cu/ZrO₂ and Co-Cu/ ZrO₂ catalysts used for ethanol steam reforming

V.S. Bergamaschi¹, F.M.S. Carvalho¹, W.R. Santos¹, C. Rodrigues¹

¹Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Centro de Química e Meio Ambiente – Laboratório de Pesquisa de Hidrogênio, Caixa Postal 11049, Pinheiros, CEP 05422-970, São Paulo, Brasil.

vsberga@ipen.br

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Abstract: Zirconia has received much attention as catalysts for its high surface area and acid-base property. The textural and acid-base properties of ZrO₂ depend on both, the synthesis procedure and the calcinations temperature. The aim of the present study is the preparation and characterization of nickel/copper/zirconia and cobalt/copper/zirconia microspheres using hydrolysis process. This process is based on homogeneous hydrolysis of droplets of a concentrated ZrO₂(NO₃)₂-urea solution after adding hexamethylenetetramine. Gelation was conducted successfully and the gel spheres were dried at 80 °C. The dried gel spheres were thermally treated at 550 °C. Characterization of the samples was performed using X-ray diffraction (XRD), BET nitrogen adsorption, scanning electron microscopy (SEM), thermogravimetric (TGA) and UV-Vis spectroscopy. The performance of the microspheres was investigated as catalysts in steam reforming of ethanol. These catalysts exhibit a good selectivity for hydrogen.

Introduction

It is known that the activity of a catalyst is greatly influenced by the method of catalyst preparation and the conditions of pretreatment [1,2]. Heterogeneous catalysts are often prepared by wet chemistry such as precipitation, co-precipitation, sol-gel or hydrolysis process.

The hydrolysis process is considered the most practical method for preparation of microspheres of various sizes. The particularly interesting method involves tethering the metal precursor to the support during the hydrolysis step, both small and large spheres may be prepared by this route [3]. These microspheres offer potential applications for high temperature catalytic reactions. In such high temperature applications, the microspheres can be used as catalyst for steam reforming of ethanol. The main advantages of this process are, to give solids with large specific surface area, high porosity, high purity and chemical composition homogeneity [4]. The solid network is formed, from the solution, via hydrolysis and condensation of molecular precursors in solution.

In recent years, increasing efforts directed towards the development of catalysts, is due to the great interest in obtain hydrogen to use in fuel cell.

Few papers dealing with ethanol steam reforming have been published up to now [5-10]. Catalytic systems based on Ni and Co catalysts seem to be most promising systems. Ni based catalyst doped with Cu using Al₂O₃ as support has been investigated by Luengo

et. al., [11] using Al_2O_3 as support. In recent work, Cavallaro et. al [12] have studied the support influence on catalytic stability of several supported catalysts. They observed that $\text{Co}/\text{Al}_2\text{O}_3$ catalysts were deactivated after 2-3 h in ethanol steam reforming (650 °C).

The catalytic behavior of supported metallic oxides is influenced by the nature of the support. The nature of metallic species in the structure of the support depends on the concentration and the temperature of the thermal treatment. Zirconia is a good porous material as catalyst support, has a high thermal stability and can be prepared with a reasonable BET surface area. [13], partly because it is chemically more stable than classic materials such as alumina and silica [14].

The aim of this work was the preparation of $\text{Ni-Cu}/\text{ZrO}_2$ and $\text{Co-Cu}/\text{ZrO}_2$ microspheres by the hydrolysis process. Characterization and evaluation of their catalytic properties in the ethanol steam reforming for hydrogen production are showed. Results were compared for both catalysts.

Experimental

Samples of $\text{Ni-Cu}/\text{ZrO}_2$ and $\text{Co-Cu}/\text{ZrO}_2$ catalysts were prepared by hydrolysis process. Zirconium nitrate (IPEN, Brazil), copper, nickel and cobalt nitrate (Merck) obtained by aqueous dissolution, were the precursor solutions used in this work.

The solution was prepared by mixing nitrate solution of copper (2 mol %), nickel or cobalt (5 mol %), urea and HMTA added into the solution of zirconium nitrate. The feed solution was dropped into silicon oil heated to about 90 °C. The gel spheres produced were washed by CCl_4 to remove silicon oil and then rinsed by 2 molar of ammonium hydroxide solution to remove by-products such as ammonium nitrate. The gel spheres were dried at 80 °C, and calcined at 550 °C, to burn out all organic compounds in the spheres.

Several techniques were used for microspheres characterizations. A scanning electron microscope (XL30, Phillips) was used to image the size microspheres, while microspheres samples were analyzed with a Mettler Toledo (TGA-851/DTA-822), for preliminary phase-transition information. The performed on the gelled spheres samples was analyzed at a heating rate of 10 °C min^{-1} from room temperature to 900 °C. The textural properties of the microspheres (specific surface area) were determined using a micrometrics ASAP-2010 instrument. X-ray investigation of the catalyst was carried out using a D8 advance, Bruker-AXS diffractometer. The UV-visible measurements of the samples were analyzed on a Varian UV-Cary-50 spectrophotometer.

Catalytic performance tests have been carried out using an apparatus which consists of a flow system, evaporator, reactor unit and the analysis system. Catalytic reactions were carried out in a fixed-bed glass reactor (i.d. = 10 mm) connected on-line to a gas chromatograph (GC Varian CP-4900), equipped with a thermal conductivity detector and two columns (molecular sieve 5A and porapak Q). The molecular sieve column was used to determine H_2 , CO and CH_4 using Ar as carrier gas, and porapak Q was used to analyze the concentration of the $\text{C}_2\text{H}_5\text{OH}$ and CO_2 , using He as carrier gas.

Results and discussion

Two catalysts were tested, changing the active phase (Cu and Ni or Co) and maintaining the oxide support (ZrO_2).

Typical SEM micrographs of these microspheres are shown in Fig. 1. Uniform and spherical shape was obtained for both catalysts Ni-Cu/ZrO₂ and Co-Cu/ZrO₂. The microspheres size were about 1,0 μm. Owing to the regular shape and nearly uniform size of the microspheres may be expected in their application fluid bed technique.

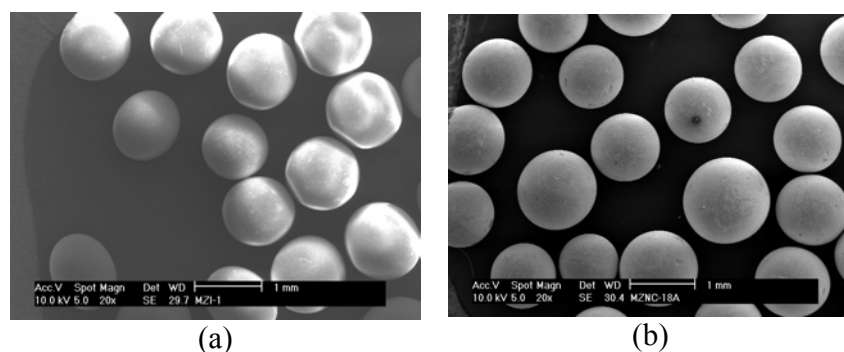


Fig. 1: SEM micrographs of typical microspheres produced by hydrolysis processes, after calcining at 550 °C for 4 h. (a) Ni-Cu/ZrO₂, (b) Co-Cu/ZrO₂.

Preliminary studies of microspheres crystallization and phase transitions of the microspheres were conducted by TGA/DTA measurements. The results of TGA and DTA were similar as showed in Fig. 2 (a) and (b).

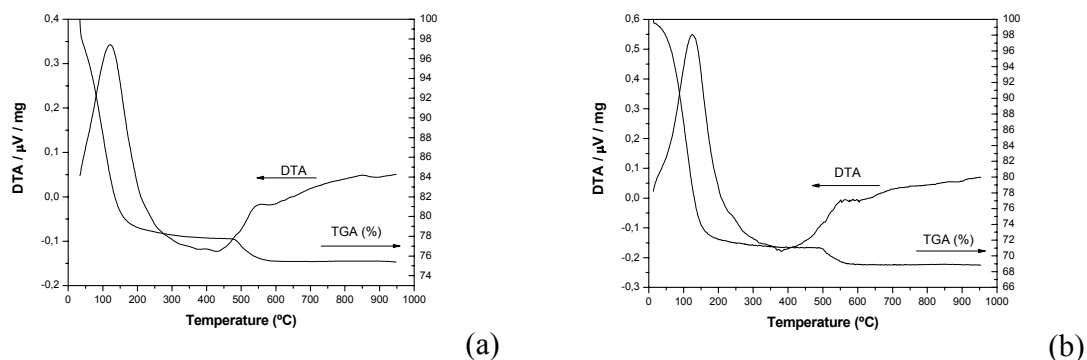


Fig. 2. Thermogravimetry (TGA) and differential thermal analysis (DTA) for microspheres. (a) Ni-Cu/ZrO₂, (b) Co-Cu/ZrO₂.

Thermal analysis of these microspheres showed a continuous loss of water up 150 °C. From 150 to 250 °C, a second step takes place, attributed to the thermal dehydration or evaporation of physically adsorbed water. From 450 °C to 550 °C a step take place attributed to the conversion of an amorphous to a crystalline phase. Endothermic reactions were observed below 500 °C. The overall mass loss was about 70,0 %. The weight decrease stops above 600 °C indicating that the loss of compounds was completed. Exothermic reactions were observed at 550 °C. These exothermic reactions were attributed to decomposition of by-products such as ammonium nitrate. The calcinations temperature of microspheres was determined to be 550 °C.

Textural properties of Ni-Cu/ZrO₂ and Co-Cu/ZrO₂ catalysts after calcinations at 550 °C and 900 °C for 4 h are presented in table 1. The results of BET measurement indicated that the specific area of catalyst Ni-Cu/ZrO₂ was 92,0 m².g⁻¹, larger than of the Co-Cu/ZrO₂ catalysts (80 m².g⁻¹). However, the difference observed in the surface area between the catalysts is relatively minor. BET surface area of the catalysts decrease with the increase of the temperature.

Table 1: BET surface area results of Ni-Cu/ZrO₂ and Co-Cu/ZrO₂.

sample	catalysts	Temperature (°C)	Surface area (m ² .g ⁻¹)
1	Ni-Cu/ZrO ₂	550	92
		900	27
2	Co-Cu/ZrO ₂	550	80
		900	25

Fig. 3 shows the XRD patterns of the calcined microspheres. The patterns show cubic zirconia as the major phase. Peak at 28,25° and 28,3° refer zirconia and exhibit monoclinic phase structure, after heat treatment at 900 °C.

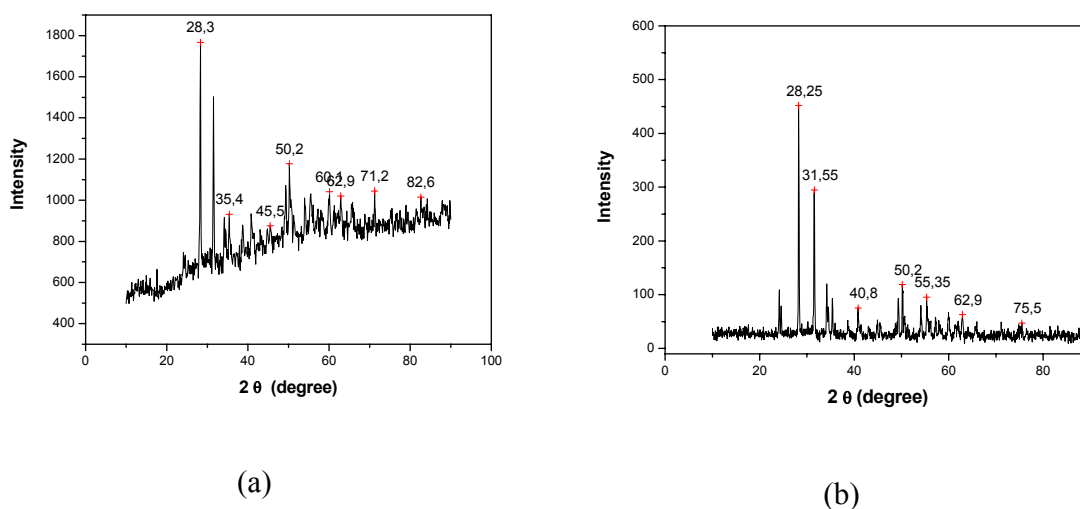


Fig. 3: X-ray diffraction pattern of microspheres calcined at temperature 900 °C for 4 h. (a) Ni-Cu/ZrO₂, (b) Co-Cu/ZrO₂.

No peak corresponding to CuO is detected; however, the existence of Cu/ZrO₂ can be not discarded. Metal oxide phase on catalysts can be certainly determined when the concentration of metals transition were than 5,0 mol %. In the samples with 5,0 mol % Ni, peaks NiO phases were observed in 2θ = 45,5°. XRD pattern for burned Co-Cu/ZrO₂ catalysts is shown in Fig. 3 (b). The presence of the intensity peak at 55,35° and 62,9° provide good evidence for assignment of the XRD features to Co₃O₄.

UV/Vis reflectance spectrum of Ni-Cu/ZrO₂ and Co-Cu/ZrO₂ catalysts in powder conditions are showed in Fig. 4. Samples activated at 550 °C showed an intense and asymmetric UV band with a maximum at 240 nm, is attributed to Zr. Additionally, weak d-

d bands of octahedrally coordinated Ni^{+2} were observed at 724, 649 and 400 nm (Fig 4a). Two strong absorption peaks in region 620 nm and 625 nm may be attributed to d-d transitions of the cobalt (II) ions (Fig 4b) and the absorption peaks in region 680 nm and 780 nm may be attributed to d-d of copper (II) ions.

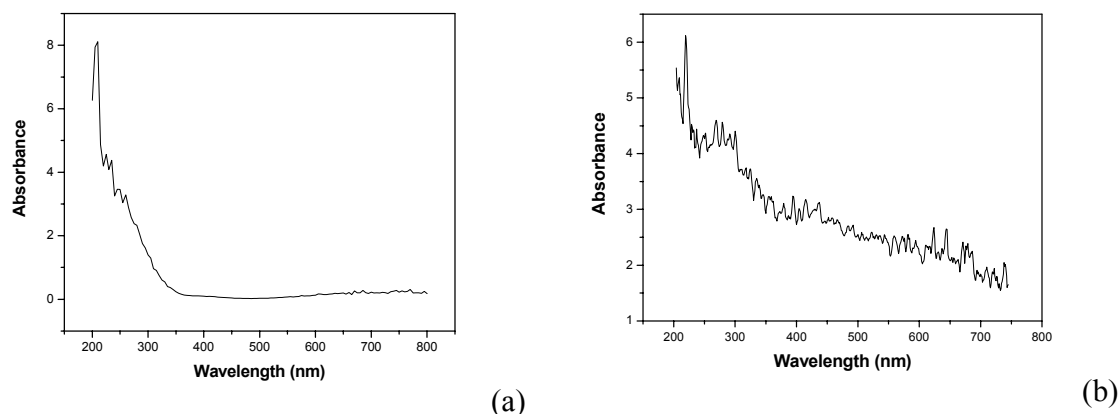


Fig. 4. DRUV-visible spectrum of microspheres: (a) Ni-Cu/ZrO₂, (b) Co-Cu/ZrO₂.

The steam reforming of ethanol was conducted with 5%Ni-2%Cu/ZrO₂ and 5%Co-2%Cu/ZrO₂ catalysts prepared by hydrolytic processes. The catalytic performance of these catalysts in the ethanol steam reforming at $T_r = 550$ °C and molar ratio 3:1 are showed in table 2.

Table 2: Steam reforming of ethanol^a

sample	catalyst	selectivity ^b			
		H ₂	CH ₄	CO	CO ₂
1	5%Ni/2%Cu/ZrO ₂	60,0	2,36	10,95	20,0
2	5%Co/2%Cu/ZrO ₂	52,0	13,63	10,28	19,0

^aReaction conditions: catalyst = 7,0 g, feed – water: ethanol = 3:1, temperature = 550 °C, conversion of ethanol 100%; ^bMolar percentage of products (water excluded).

Ethanol is totally converted in the temperature of 550 °C. The results also indicate that Ni-Cu/ZrO₂ catalysts show significant activity for the reforming reaction and are more selective to hydrogen than Co-Cu/ZrO₂ catalysts. This is attributed largely to the combined activities of Ni (in breaking the C-C bond) and the dispersed Cu⁺² (responsible for the catalytic activity) on ZrO₂. Hydrogen is the main constituent of the reaction effluent, which also contains CH₄, CO and CO₂. The support precursor (ZrO₂) is highly stable for both catalysts. Nickel/copper catalysts exhibit higher activity and selectivity to H₂ (60 %) than cobalt/copper catalysts (52%).

Conclusions

The experimental results let assess that spherical catalysts can be produced by hydrolysis processes with larger specific area (92 m².g⁻¹) calcined in temperature 550 °C.

Stems reforming of ethanol using Ni-Cu/ZrO₂ and Co-Cu/ZrO₂ catalysts, were investigated to examine the activity and selectivity. A hydrogen-rich gas mixture in temperature 550 °C and H₂O/EtOH molar ratio 3:1 was produced. Both catalysts possessed high activity and good stability.

The catalyst of 5%Ni-2%Cu/ZrO₂ composition exhibited most stable activity in long-term experiments without changing in selectivity for hydrogen and is a good choice to use in ethanol steam reforming processors for fuel cell applications. Ni-Cu/ZrO₂ and Co-Cu/ZrO₂ catalysts performance still will be subject for further researches.

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