



## Ethanol reforming and partial oxidation with Cu/Nb<sub>2</sub>O<sub>5</sub> catalyst

Carlos E.M. Guarido<sup>a</sup>, Deborah V. Cesar<sup>a</sup>, Mariana M.V.M. Souza<sup>a,b</sup>, Martin Schmal<sup>a,\*</sup>

<sup>a</sup> NUCAT/PEQ/COPPE - Federal University of Rio de Janeiro/UFRJ, Centro de Tecnologia, Bloco G, sala 128, CEP 21945-970, Rio de Janeiro/RJ, Brazil

<sup>b</sup> Escola de Química - UFRJ, Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909, Rio de Janeiro/RJ, Brazil

### ARTICLE INFO

#### Article history:

Available online 24 September 2008

#### Keywords:

Ethanol  
Reforming  
Hydrogen  
Copper  
Niobia

### ABSTRACT

Ethanol reforming and partial oxidation were studied on Cu/Nb<sub>2</sub>O<sub>5</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. Compared to the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, the Cu/Nb<sub>2</sub>O<sub>5</sub> catalyst presents conversion as high as Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, however, for the same level of formation of hydrogen it occurs at much lower temperature on the Cu/Nb<sub>2</sub>O<sub>5</sub> catalyst, 200 °C lower than for the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, with remarkable little formation of CO, which can be attributed to the strong interaction between copper and niobia. Temperature-programmed desorption (TPD-ethanol) and surface reactions (TPSR) of partial oxidation of ethanol showed formation of ethylene, acetaldehyde, ethane and mainly H<sub>2</sub> and CO<sub>2</sub> besides little methane. DRIFTS results are in accordance with TPD analysis and the formation of acetate species at room temperature suggests reactivity of the surface and its oxidative dehydrogenation capacity. The adsorption of ethanol gives rise to ethoxide species, which form acetate and acetaldehyde that can be oxidized to CO<sub>2</sub> via carbonate. A comparison with reported results for Cu/Al<sub>2</sub>O<sub>3</sub> this catalyst is promising, yielding high level of H<sub>2</sub> with little CO production during reforming and partial oxidation reaction. The maximum H<sub>2</sub> formation for the partial oxidation of ethanol was 41% at ratio (O<sub>2</sub>/Et) 0.8, increasing to 50% at ratio 1.5. The H<sub>2</sub>/CO is around 10 for the partial oxidation and 7 for steam reforming, which is excellent, compared to the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with a factor 4–8 lower.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Nowadays, increasing attention is being paid to pollution-related environmental and public health problems. Particularly, as one of the major contributor to the atmospheric pollution, the automotive section had to work hard on pollution control. Both catalytic converters on gasoline-fueled engines and filters for particulates on diesel-fueled engines were implemented.

The next step, to overpass the forthcoming regulations on CO<sub>2</sub> emissions according to the Kyoto's Protocol (in Europe, 8% reduction compared to the 1990s emissions by 2008–2012, EUA 7%), requires the development of both new engines and alternative fuels [1].

Bio-ethanol, presented as an environmentally fuel (renewable, CO<sub>2</sub> neutral, non-toxic), is used in catalytic steam reforming reaction or partial oxidation for H<sub>2</sub> onboard production.

Thermodynamically these reactions are possible; however, the great challenge is to find out catalysts with high stability, active and mainly selective for hydrogen. In addition, these catalysts must be resistant to coke formation. The interest for hydrogen production

from ethanol has increased in the last years, and there are some new catalysts with different metals and supports [2–5].

Auprêtre et al. [6] studied catalysts for reforming of ethanol with high selectivity to CO<sub>2</sub> (minimum CO formation) with a series of metals (Rh, Pt, Pd, Ru, Ni, Cu, Zn, Fe) and different supports (Al<sub>2</sub>O<sub>3</sub>, 12% CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CeO<sub>2</sub>–ZrO<sub>2</sub>, ZrO<sub>2</sub>). Ni and Rh supported on alumina were the most promising catalysts in terms of activity and selectivity and the activity depends directly on the decreasing mobility of OH groups at the surface. The activity follows in decreasing order: Rh ≥ Ni > Pd > Pt > Cu = Zn > Ru = Fe.

Alberton et al. [7] studied steam reforming over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts varying the Ni content (8 and 16%) and the support (α and γ/alumina) and analyzed the effect of activation on the activity and carbon formation. As reported the activation method affected the stability and the nature of carbon influenced the stability.

Cavallaro and Freni [8] studied the ethanol reforming with mixed oxide catalyst CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, showing that the main products CO, CO<sub>2</sub> and H<sub>2</sub> are formed above 350 °C. Cooper supported on alumina was studied in the ethanol reforming, showing that copper promoted a rapid dehydrogenation of ethanol to acetic aldehyde, while nickel favored the rupture of carbon–carbon bonds of ethanol, with formation of methane and carbon monoxide [9].

Niobium oxide is a reducible material and presents strong metal support interaction, depending of the reduction temperature

\* Corresponding author. Fax: +55 21 25628360.

E-mail address: [schmal@peq.coppe.ufrj.br](mailto:schmal@peq.coppe.ufrj.br) (M. Schmal).