



Hydrogen production by aqueous-phase reforming of ethanol over nickel catalysts prepared from hydrotalcite precursors

Ivna O. Cruz^a, Nielson F.P. Ribeiro^b, Donato A.G. Aranda^a, Mariana M.V.M. Souza^{a,b,*}

^aEscola de Química – UFRJ, Centro de Tecnologia, Bloco E, sala 206, CEP 21949-900 Rio de Janeiro/RJ, Brazil

^bNUCAT/PEQ/COPPE – UFRJ, Centro de Tecnologia, Bloco G, sala 128, CEP 21945-970, Rio de Janeiro/RJ, Brazil

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ABSTRACT

Derived hydrotalcite catalysts, with different Ni loadings, were prepared and tested in aqueous-phase reforming of ethanol. Upon calcination of the hydrotalcite-like compounds, there was formation of MgO periclase-type phase, where both nickel and aluminum oxides are well dispersed. The mixed oxides showed only one reduction peak in temperature range of 900–1000 °C. The catalytic tests were carried out in a batch reactor with an aqueous solution of 1 wt.% ethanol at different temperatures (200, 230 and 250 °C). The derived hydrotalcite catalysts showed high activity, with 65% of ethanol conversion at 230 °C, high hydrogen selectivity and lower methane production than alumina supported nickel catalyst.

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1. Introduction

The depletion of the fossil fuels reserves and the impact on the environment lead to an increasing interest in a sustainable development. In recent years, there are many researches in new sources of energy, especially clean energy. Hydrogen is an attractive alternative that can be produced from renewable resources, such as biomass.

Aqueous-phase reforming (APR) of oxygenated compounds derived from biomass to produce H₂ has several advantages. It can be carried out at low temperatures, reducing the cost of the process because it is not necessary to vaporize water and minimizing undesirable decomposition reactions. Furthermore, it is possible to generate H₂ and CO₂ in a single step with low levels of CO [1].

Many oxygenated compounds, such as methanol, sorbitol, glycerol and ethyleneglycol, have been used in APR process [1–3]. Ethanol, produced by fermentation of biomass, such as sugar cane, is an attractive source of H₂ because of its high hydrogen content, non-toxicity and safe storage. Moreover, the hydrogen production process from ethanol is a CO₂ free cycle, because the CO₂ generated in reforming is consumed by photosynthesis during biomass growth. Brazil is the world leader of ethanol production from sugar

cane and has an advanced technology to produce, distribute and transport ethanol.

Supported Pt, Ni, Ru, Rh, Pd and Ir [1–5] catalysts have been tested in APR process and have shown good activity and selectivity for H₂ production. The mechanism of H₂ production from ethylene glycol was described by Shabaker et al. [3,6]. The process involves the cleavage of C–C bonds as well as C–H bonds to form adsorbed species (especially CO) on the catalyst surface. CO is converted in H₂ and CO₂ by the water–gas shift reaction. In addition, more H₂ could be produced from ethylene glycol dehydrogenation. Thus, a good catalyst for APR process has to be active in the cleavage of C–C bonds and water–gas shift reaction, but has to inhibit the cleavage of C–O bond and methanation reactions. Ni shows a good activity for C–C scission followed by water–gas shift reaction, but it also exhibits high rates of methanation [1]. Dumesic research group [4,6,7] reported that addition of Sn to Ni catalysts increases the selectivity for hydrogen production by decreasing the selectivity toward the formation of alkanes.

Hydrotalcite-like compounds (HTLCs) are anionic clays, layered double hydroxides with lamellar structure, showing interesting properties, such as large surface area, “memory effect” and basic character [8]. Upon heating, these compounds form a homogeneous mixture of oxides with very small crystal size, stable against thermal treatments, which by reduction result in high dispersion of the metallic crystallites. Ni–Mg–Al mixed oxides derived from hydrotalcite precursors have been used as catalysts for various reactions, with high activity and low coke formation [9–11].

* Corresponding author. Address: Escola de Química – UFRJ, Centro de Tecnologia, Bloco E, sala 206, CEP 21949-900 Rio de Janeiro/RJ, Brazil. Tel.: +55 21 25627640; fax: +55 21 25627596.

E-mail address: mmattos@eq.ufrj.br (M.M.V.M. Souza).