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Mg and Al mixed oxides and the synthesis of *n*-butanol from ethanol

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ABSTRACT

n-Butanol is used in a wide range of applications, especially for the production of paint, solvents and plasticizers. Recently, some companies have proposed the use of *n*-butanol as a fuel, which can be employed pure or blended with gasoline or diesel. At present, there is great interest in developing a one-step process that generates *n*-butanol from ethanol. Some works showed that Mg–Al mixed oxides are very promising catalysts for this matter. Analyzing the physical–chemical properties of these catalysts, this work aims at further studying this reaction. The Mg–Al mixed oxides were obtained by thermal decomposition of hydrotalcites employing two Mg/Al different ratios. Magnesium oxide (MgO) and alumina (Al_2O_3) were also prepared following the same synthetic route used for the Mg–Al mixed oxides. The synthesized samples were characterized by the following techniques: XRD, NMR, BET and XRF. The acid and basic properties of the samples were also analyzed employing probe molecules. The catalytic tests were performed using a fixed bed reactor at atmospheric pressure. It was verified that the Mg and Al mixed oxides are able to promote the synthesis of C4 compounds from ethanol. Adjacent acid and medium basic sites are needed in order to generate the intermediate compounds. These pairs of acid and medium basic sites are obtained by the insertion of Al in the MgO lattice or in consequence of the presence of Mg in the γ-Al_2O_3 lattice. It was observed that the higher the concentration of Mg is, the higher the hydrogenation capacity of the catalyst, since a greater selectivity to *n*-butanol was observed. Strong basic sites and a specific superficial atomic arrangement seem not to be essential for the synthesis of C4 from ethanol.

1. Introduction

Nowadays, many companies are showing a growing interest in investments focused on sustainable business from an economical, environmental and social standpoint. In relation to the Chemical Industry, special emphasis has been given to the use of renewable raw material (biomass) for the generation of final or intermediate products. According to this new picture, ethanol stands out as an important industrial raw material. Brazil and the US are in a position of great advantage due to the sheer volume of ethanol produced in these countries.

Recently, some companies have proposed the use of *n*-butanol as fuel. This new application is associated with some properties among which the energetic value of *n*-butanol (29.2 MJ/L) stands out since it is higher than the one of ethanol (19.6 MJ/L). This compound can also be used in a wide range of applications, especially for the production of paint, solvents and plasticizers [1–3].

The Oxo process is the most employed one for the *n*-butanol synthesis. It involves several reaction steps, some of which use homogeneous catalysts and non-renewable resources such as propylene and CO [3].

At present, there is great interest in developing a one-step process that generates *n*-butanol from ethanol. This synthesis would be carried out using only one reactor where the dehydrogenation of ethanol would occur producing acetaldehyde. After that, two molecules of this aldehyde would be condensed generating acetaldol (3-hydroxybutyraldehyde), which would then be dehydrated and hydrogenated producing *n*-butanol [4].

So far, the two most promising catalytic systems, which have been proposed regarding this synthesis are the following: the hydroxyapatites and the mixed oxides obtained from hydrotalcites composed of Mg and Al [4–10]. The first system shows high selectivity to *n*-butanol at low conversion levels [5,6]. However, at high conversions, hydroxyapatites generate compounds with high molecular weight, which provoke the deactivation of these catalysts. On the other hand, the mixed oxides are less active than the first ones, and as a result, they generate less heavy compounds. Thus, the deactivation rate is much lower.

León et al. [9] employing Mg–Al mixed oxides suggested that the catalytic systems that show high density of strong basic sites are the most selective to *n*-butanol. They also observed a very high selectivity to ethylene, which is associated with the presence of acid

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