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Zirconia supported Cu systems as catalysts for n-butanol conversion to butyraldehyde

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ABSTRACT

A promising alternative for the production of butyraldehyde is the use of n-butanol as raw material. This alcohol can be produced via fermentation from renewable resources. n-Butanol can be converted to butyraldehyde by dehydrogenation or by partial oxidation and for both reactions Cu catalysts show activity. In this work, Cu supported on both pure ZrO_2 and ZrO_2 modified with CeO_2 catalysts were studied in these two catalytic reactions. The catalytic performance and the catalysts characterization (ICP, N_2-physisorption, XRD, TPR, and XPS) suggest that the catalyst with the best Cu dispersion was the most active and stable in n-butanol dehydrogenation. However, in n-butanol partial oxidation, the initial dispersion of Cu on the supports is deteriorated during the time on stream, being Cu sintering and oxidation the main causes of the lower butyraldehyde yield observed in this catalytic process.

1. Introduction

Aldehydes are important industrial intermediates for the production of fine chemicals and specialities [1]. Moreover, these chemicals can be converted into oxygenated fuel additives, such as acetals, or synthetic resins. Aldehydes are also used as accelerators in rubber vulcanization, solvents and plasticizers [2]. In general, these are commercially produced by alkenes hydroformylation. Nevertheless, another commonly method of aldehyde production is alcohol oxidation, which is very attractive if alcohols derived from biomass are used. These bioalcohols will become an attractive, economic and sustainable alternative for fuel additives or for other products generation due to decreasing oil reserves and limitations in green house gases emissions to the atmosphere. However, the process for aldehyde production through alcohol oxidation uses a toxic inorganic salt; therefore it is necessary to eliminate this salt from the final stream to obtain the desired product [1]. Due to these environment and economic concerns, new routes for aldehyde production are being investigated. One of the most promising alternatives for aldehyde production is the selective catalytic partial oxidation. This process using environmentally benign oxidants has been developed in recent years [3–5]. In most of cases, this alcohol oxidation takes place in liquid phase [1–4], and the presence of a solvent is usually necessary to favor the alcohol oxidation [6]. Hence, the development of new and better processes seems necessary. In this sense, catalytic processes based on the dehydrogenation or partial oxidation of bioalcohols without additional solvents may be a way more consistent with the current environmental policies. Both processes, gas phase dehydrogenation or partial oxidation, present the advantage of much simpler subsequent purification stages.

For liquid phase alcohol oxidation, different catalysts have been studied, for example, Cu-based catalysts [7], Co-based [8,9] and noble metal-based catalysts such as Ru, Pd and Os, among others [10–12]. Even if several studies have been published about the production of aldehydes in the presence of noble and non noble metals in liquid phase, the butyraldehyde gas phase production without solvent has not yet been reported. Hence, the main objective of this work is to compare the production of butyraldehyde by using both catalytic routes: n-butanol partial oxidation and n-butanol dehydrogenation. For this purpose, different copper catalysts supported on ZrO_2 and ZrO_2 modified with CeO_2 were prepared, characterized and tested in the about mentioned catalytic processes.

2. Experimental

2.1. Catalyst preparation

Support materials used were: zirconium dioxide (Magnesium Elektron Ltd., zirconium hydroxide (silica stab)) and zirconium

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