



Gas phase hydrogenation of maleic anhydride at low pressure over silica-supported cobalt and nickel catalysts

Camilo I. Meyer¹, Silvina A. Regenhardt, Alberto J. Marchi, Teresita F. Garetto*

Catalysis Science and Engineering Research Group (GICIC), Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), FIQ-UNL-CONICET, Santiago del Estero 2654 (3000) Santa Fe, Argentina

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ABSTRACT

The gas-phase hydrogenation of maleic anhydride over Ni/SiO₂ and Co/SiO₂ catalysts, prepared by the incipient wetness impregnation method, was studied. The catalytic tests were carried out at 1 bar pressure, between 170 and 220 °C and W/F_{MA}^0 in the range 5–25 g h mol⁻¹. In this work, the product distribution was different to those obtained at high pressures, previously reported in the open literature. Both Ni/SiO₂ and Co/SiO₂ catalysts were active for the selective hydrogenation of maleic anhydride (MA) into succinic anhydride (SA). Subsequently, SA was converted to γ -butyrolactone (GBL) and propionic acid (PA). Neither tetrahydrofuran nor butanediol were detected at the reactor outlet. GBL/PA ratio was strongly depending on the metallic catalyst and temperature. At 170 °C, Ni/SiO₂ was more selective to GBL than Co/SiO₂. Besides, with Ni/SiO₂, GBL formation rate diminished during the experiment while PA production showed a small increase. Instead, over Co/SiO₂, both the PA and GBL formation rate decayed with time on stream. At 220 °C, Co/SiO₂ showed a higher initial selectivity to GBL than Ni/SiO₂. However, the GBL formation rate diminished more rapidly with Co/SiO₂ than with Ni/SiO₂. Thus, both catalysts gave similar selectivity to GBL after 3 h reaction at 220 °C. The observed catalyst deactivation was attributed to carbonaceous species of different nature deposited on the metallic phase during reaction. The amount and type of these species depends on both metal catalysts and reaction conditions. Selectivity and stability of Ni/SiO₂ and Co/SiO₂ catalysts is explained on the basis of their hydrogenolytic activity.

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1. Introduction

The main products in the gas phase hydrogenation of maleic anhydride (MA) are succinic anhydride (SA), γ -butyrolactone (GBL), tetrahydrofuran (THF) and butanediol (BDO). The reaction network for the gas-phase MA hydrogenation is rather complex and different type of reactions can occur, depending on the catalyst and reaction conditions [1,2]. In a first step, the hydrogenation of the C=C bond in MA produces SA. Then, the hydrogenolysis of one C=O bond in SA gives GBL. Finally, THF and BDO can be obtained by GBL hydrogenolysis. Other hydrogenolysis reactions can also produce C₄ and C₃ compounds, such as *n*-butanol, *n*-propanol, butyric acid and propionic acid (PA). Most of the compounds mentioned above are mainly employed as solvents, especially to replace the non eco-friendly chlorinated solvents. GBL, PA, THF and BDO are important intermediates in the chemical industry, as well. For example, GBL is used in the synthesis of pyrrolidone and *N*-methylpyrrolidone,

which are employed for production of agrochemicals, pharmaceuticals and polymers. THF, BDO and PA are used as intermediates for the production of polymers, pesticides and pharmaceuticals. PA is also employed as mold and bacteria inhibitor for animal feed and human food [3,4].

The use of different catalysts, based on both noble and non-noble metals, was reported in the literature for the hydrogenation of MA [1–5,8–24]. Copper-based catalysts modified by Zn, Cr, Ce and Zr were employed for the MA hydrogenation in gas phase [6,7,12,13]. However, Cu loadings as high as 40–60%, high catalyst/reactive ratios and/or high pressures were necessary to obtain high GBL yields. In addition, Cr-based catalysts are not desirable due to the high toxicity of this metal. The liquid-phase hydrogenation of MA was widely studied and high pressures and high temperatures are required to obtain yields in GBL near 40–50% [2,10,14–19].

In a previous paper, we reported the gas-phase hydrogenation of MA over Cu(10%)/SiO₂, prepared by the incipient-wetness impregnation method, at 1 bar and 170–220 °C. After activation under H₂ flow, a phase formed by large metal copper particles was obtained. This catalyst was active and selective in the hydrogenation of MA into SA. However, only very small amounts of GBL were obtained through hydrogenolysis of SA. Besides, this catalyst suffered a rapid

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: tgaretto@fiq.unl.edu.ar (T.F. Garetto).

¹ Present address: Instituto de Desarrollo Tecnológico para la Industria Química (INTEC) UNL-CONICET.