



# Selective gas phase hydrogenation of maleic anhydride over Ni-supported catalysts: Effect of support on the catalytic performance

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## ABSTRACT

The gas phase hydrogenation of maleic anhydride to obtain  $\gamma$ -butyrolactone was studied using Ni supported on  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and zeolite H-BEA as catalysts. The samples were prepared by incipient wetness impregnation and characterized by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  (Sg), X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption of  $\text{NH}_3$  (TPD- $\text{NH}_3$ ) and chemisorption of  $\text{H}_2$ . The reaction was carried out at  $170^\circ\text{C}$  and  $220^\circ\text{C}$  in a fixed bed reactor operating at atmospheric pressure. From the characterization results, it was determined that the degree of  $\text{Ni}^{2+}$ -support interaction varies according to the following pattern:  $\text{Ni/HBEA} > \text{Ni/SiO}_2\text{-Al}_2\text{O}_3 > \text{Ni/SiO}_2$ . All catalysts were very active in the hydrogenation of maleic anhydride to succinic anhydride. However, hydrogenolytic activity and stability of nickel-based catalyst varies with the degree of interaction  $\text{Ni}^{2+}$ -support. Ni/H-BEA, in which  $\text{Ni}^{2+}$ -support interaction is the highest, was active in the hydrogenolysis of succinic anhydride to  $\gamma$ -butyrolactone but it was not stable. By contrast,  $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$  and  $\text{Ni/SiO}_2$ , with medium or low degree of  $\text{Ni}^{2+}$ -support interaction, were more stable than Ni/H-BEA. In addition,  $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ , with a medium degree of  $\text{Ni}^{2+}$ -support interaction, was the most stable and selective to  $\gamma$ -butyrolactone, especially when the reaction was carried out at  $220^\circ\text{C}$ .

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## 1. Introduction

The global reaction network for maleic anhydride (MA) hydrogenation over Ni-based catalysts is shown in Fig. 1. In this process, both hydrogenation and hydrogenolysis reactions are involved. Some of the possible reaction products, as succinic anhydride (SA),  $\gamma$ -gammabutyrolactone (GBL), tetrahydrofuran (THF), and 1,4-butanediol (BDO), are important starting materials in chemical industry. In particular, SA, the first product in the reaction sequence, is widely used in the manufacture of polymeric materials, pharmaceuticals, agrochemicals, dyes, photographic chemicals, surface active agents, lubricant additives, organic flame retardant materials, esters, flavors and fragrances. GBL is mainly used as solvent in replacement of chlorinated solvents and synthesis intermediate for the production of agrochemicals, pharmaceuticals and polymers [1,2].

In the open literature, several papers reported different type of catalysts and a variety of operating conditions in order to carry out the MA hydrogenation [1–10]. The reaction was studied using several types of noble metal-based catalysts, such as Pd, Pt and

Au, both in liquid and gas phase [3,7–9]. Generally, the experiments were carried out in the temperature and pressure ranges of  $190\text{--}240^\circ\text{C}$  and  $1\text{--}5\text{ MPa}$ , respectively. Copper-based catalysts were also used to study the gas-phase hydrogenation of MA between  $210$  and  $280^\circ\text{C}$  [4,10]. In general, the catalysts composition of these copper-based catalysts is rather complex since they also contain Al, Zn, Cr and Ce. In addition, the use of Cr-based catalysts is undesirable because hexavalent Cr ions are highly toxic. In all of the cases, the main products were SA, GBL, THF and BDO and the product distribution was strongly depending on the reaction conditions and the type of catalyst. Other by-products may also be obtained during MA hydrogenation, such as propionic acid (PA), methane and CO [5,6]. In some cases, partial catalyst deactivation has been reported for copper-based catalysts [10–12].

Despite the fact that there are many works in which an exhaustive study of the behavior of Ni, supported on mesoporous and microporous solids, in different hydrogenation–hydrogenolysis reactions was made [13,14], to our knowledge, there is not research work dealing with the study of support influence on the performance of Ni-based catalysts in the gas phase MA hydrogenation.

In a previous work we found evidence that Ni-based catalysts are active for MA hydrogenation and SA hydrogenolysis in gas phase [15]. In this work, we analyze the catalytic performance of Ni supported over different insulating oxides on the selective MA hydrogenation to GBL in gas phase at atmospheric pressure. The

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