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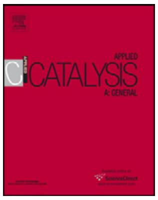

Selective hydrogenation of maleic anhydride to succinic anhydride catalyzed by metallic nickel catalysts

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ABSTRACT

Maleic anhydride was selectively hydrogenated to succinic anhydride over metallic nickel catalysts, such as Raney Ni and Ni nanoparticles, in liquid phase at reaction temperature lower than 130 °C. When the Raney Ni catalyst in solvents with different polarities catalyzed the hydrogenation of maleic anhydride to succinic anhydride, the solvent with high polarity favored the hydrogenation of maleic anhydride to succinic anhydride as compared to that with low polarity. When the hydrogenation reaction was catalyzed by Raney Ni catalyst at 100 °C and H_2 pressure of 2.5 MPa for 360 min in acetic anhydride, the conversion of maleic anhydride and the selectivity of succinic anhydride were 99.6% and 100%, respectively. In solvent-free reaction system, γ-butyrolactone as a byproduct with the maximum selectivity of 14.8% was produced at 130 °C. All of the Ni nanoparticles with average diameters ranging from 8 to 313 nm showed higher catalytic activity than Raney Ni in liquid phase hydrogenation of maleic anhydride to succinic anhydride. When the Ni nanoparticles with an average diameter of 8 nm were used as the catalysts in the liquid phase hydrogenation at 80 °C and 2 MPa of H_2 for 150 min and the weight ratio of catalyst to maleic anhydride was 1:100, the conversion of maleic anhydride and the selectivity of succinic anhydride were 99.8% and 100%, respectively. The small particle size and the polycrystalline structure of Ni nanoparticles played important roles in the liquid phase selective hydrogenation of maleic anhydride to succinic anhydride.

1. Introduction

Maleic anhydride (MA) has been considered as a good feedstock since MA can be produced at a low cost and on a large scale by partial oxidation of *n*-butane instead of benzene now [1–3]. Catalytic hydrogenation of MA produces important industrial chemicals, such as succinic anhydride (SA), γ-butyrolacetone, tetrahydrofuran and 1,4-butanediol, which are widely used in polymer and pharmaceutical industries. From among the derivatives of MA, SA is typically used in the manufacturing of pharmaceuticals, agrochemicals, and polymers [4].

SA is traditionally produced by the dehydration of succinic acid, which is produced by electrochemical reduction of MA. Catalytic hydrogenation of MA to SA is an alternative to the traditional process, in viewpoint of lowering cost and environmental protection.

Hydrogenation of MA can be catalyzed by transition metals in both liquid and gas phases. It was reported that when Pd-Sn/SiO_2 [5], Pd/SiO_2 [6], and Pd-Mo-Ni/SiO_2 [7] catalyzed the liquid phase hydrogenation of MA at 220–260 °C and 5–8 MPa of H_2, γ-butyrolactone was dominantly formed. Supported copper catalysts, such as Cu/ZnO/Al_2O_3 [8–10], Cu/CeO_2/Al_2O_3 [11], Cu/ZnO/TiO_2 [12], and Cu/ZnO/ZrO_2 [13], favored the formation of γ-butyrolactone and tetrahydrofuran in the gas phase hydrogenation of MA at 220–280 °C and 0.03–1 MPa of H_2. High temperature and H_2 pressure are beneficial to the hydrogenation of MA to tetrahydrofuran *via* consecutive hydrogenation of MA to SA, SA to γ-butyrolactone, and γ-butyrolactone to tetrahydrofuran. SA is an intermediate product during the catalytic hydrogenation of MA since the double bonds in MA molecules are easily hydrogenated by H_2.

Several research groups investigated selective hydrogenation of MA to SA. When $RhCl(PPh_3)_3$ complex was used as the catalyst in ethylene glycol dimethylether, the yield of SA reached 99.0% at 110 °C and 2.5 MPa of H_2 [14]. When MA hydrogenation was carried out over Pd/Al_2O_3 in supercritical CO_2 medium, SA was dominantly formed at low temperature of 100 °C [15]. When Ru-Ni/SiO_2 was used as the catalyst in tetrahydrofuran at 240 °C and 7 MPa of H_2, SA was produced as the main product (73.2 wt%) in accompany with the formation of γ-butyrolactone and 1,4-butandiol [7]. In order to avoid the utilization of expensive noble metal catalysts and inconvenient batch reaction system, copper-based catalysts were investigated in gas phase hydrogenation of MA and in fixed bed

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