

Oxidative Dehydrogenation and Hydrogenation of Malic Acid over Transition Metal Oxides

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Abstract : Oxidative dehydrogenation and hydrogenation reactions of L-malic acid are interesting ways for its transformation into valuable products, including oxaloacetic, pyruvic and malonic acids but also 1,4-butanediol and 1,2,4-butanetriol. Keto acids have a range of applications in many chemical syntheses as pharmaceuticals, food additives and cosmetics. 3-Hydroxybutyrolactone and 1,2,4-butanetriol are used for the synthesis of chiral pharmaceuticals and other fine chemicals, while 1,4-butanediol can be used for organic syntheses, such as polybutylene succinate (PBS), polybutylene terephthalate (PBT), and for production of tetrahydrofuran (THF). L-malic acid is a non-toxic and natural organic acid present in fruits, and it is the main component of wine alongside tartaric acid representing about 90% of the wine total acidity. Iron oxides doped with cobalt ($\text{Co}_x\text{Fe}_{3-x}\text{O}_4$; $x = 0; 0.05; 0.1; 0.15$) were studied as catalysts in these reactions. There is no mention in the literature of non-noble transition metal catalysts for these reactions. The method used for catalysts preparation was coprecipitation, while BET XRD, XPS, FTIR and UV-VIS spectroscopy were used for the physicochemical properties evaluation. The XRD patterns revealed the presence of $\alpha\text{-Fe}_2\text{O}_3$ rhombohedral hematite structure, with cobalt atoms well dispersed and embedded in this structure. The studied samples are highly crystalline, with a crystallite size ranged from 58 to 65 nm. The optical absorption properties were investigated using UV-Vis spectroscopy, emphasizing the presence of bands that correspond with the reported hematite nanoparticle. Likewise, the presence of bands corresponding to lattice vibration of hexagonal hematite structure has been evidenced in DRIFT spectra. Oxidative dehydrogenation of malic acid was studied using as solvents for malic acid ethanol or water (2, 5 and 10% malic acid in 5 mL solvent) at room temperature, while the hydrogenation reaction was evaluated in water as solvent (5%), in the presence of 1% catalyst. The oxidation of malic acid into oxaloacetic acid is the first step, after that, oxaloacetic acid is rapidly decarboxylated to malonic acid or pyruvic acid, depending on the active site. The concentration of malic acid in solution, in turn, has an influence on conversion; this decreases when the concentration of malic acid in the solution is high. The spent catalysts after the oxidative dehydrogenation of malic acid in ethanol were characterized by DRIFT spectroscopy and the presence of oxaloacetic, pyruvic and malonic acids, along with unreacted malic acid were observed on the surface. The increase of the ratio of Co/Fe on the surface has an influence on the malic acid conversion and on the pyruvic acid yield, while the yield of malonic acid is influenced by the percentage of iron on the surface (determined from XPS). Oxaloacetic acid yield reaches a maximum at one hour of reaction, being higher when ethanol is used as a solvent, after which it suddenly decreases. The hydrogenation of malic acid occurs by consecutive reactions with the production of 3-hydroxy-butyrolactone, 1,2,4-butanetriol and 1,4-butanediol. Malic acid conversion increases with cobalt loading increasing up to Co/Fe ratio of 0.1, after which it has a slight decrease, while the yield in 1,4-butanediol is directly proportional to the cobalt content.

Keywords : malic acid, oxidative dehydrogenation, hydrogenation, oxaloacetic acid

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