



ÁREA: Catálise ambiental, fotocatálise e eletrocatalise

Chemical recycling of polyethylene terephthalate via glycolysis over NiMnAl catalysts: A comparison between coprecipitation and urea synthesis method

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Resumo-Abstract

The reuse of Poly (ethylene terephthalate) - PET post-consumer residues is generally performed by mechanical processes. However, the quality of the resulting PET decreases after a limited number of reuses. Therefore, chemical “recycling”, especially glycolysis with ethylene glycol, allowing the formation of the monomer bis-2-hydroxy-ethyl terephthalate (BHET) is a useful alternative and the monomer can be used again to obtain higher PET purity. Nevertheless, the glycolysis reaction needs a catalyst, and heterogeneous materials have great interest since they promote easier separation and less BHET product contamination. Still, trimetallic combinations of mixed oxides are yet to be explored [1]. This study aimed to compare the influence of catalyst synthesis by coprecipitation and urea method on the properties of mixed oxides of Ni, Mn, and Al and their activity in PET glycolysis. The coprecipitation was conducted at a constant pH of 9 and 65°C. The precipitate was aged for 4h at 65°C and 18h at 25°C [2]. In the urea method, water, metal chlorides, ethylene glycol (EG), and urea were submitted to reflux (~90°C) for 24h and 18h at room temperature [3]. The precipitates in both methods were filtered, washed with boiling water, dried, and calcined at 600°C to obtain the catalysts. The precursors and catalysts were analyzed through XRD, TGA, FTIR, EDX, and N₂ adsorption/desorption. The glycolysis tests were performed at 196°C, following a procedure described in [4], using a mass ratio EG: PET = 5:1, and catalyst: PET ratio of 0,005. The XRD results showed for the precursors a pattern associated with hydrotalcite and hausmannite (Mn₃O₄) for coprecipitation materials and rhodochrosite (MnCO₃) for urea method. The catalyst prepared by the urea method displayed more crystalline phases like Mn₂O₃ than those resulting from the coprecipitation method. Nickel and aluminum were found in the NiO/NiAl₂O₄ phases. TGA and FTIR analyses corroborated that the precursors present the hydrotalcite phase and show an additional thermal transition related to the manganese oxidation into Mn₂O₃ in the case of the urea method. The specific surface area of the catalyst after the coprecipitation (170m²/g) was greater than that of the urea method (120 m²/g). The experimental composition of the mixed oxides was close to the theoretical one: Ni_{0.22}Mn_{0.45}Al_{0.33}. Both catalysts displayed high activity, 100% PET conversion, and 85% BHET yield after 40 min reaction. This result shows that the synthesis method did not influence their catalytic properties, being then interchangeable. However, the coprecipitation presented three advantages over the urea method: i) its synthesis time is 24h against 42h, ii) the catalyst yield is greater, iii) the specific surface area is higher.

Palavras-chave: recycling; PET; glycolysis; nickel; manganese; aluminium; coprecipitation; urea method

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