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Glycerol conversion to acrolein over Nb_2O_5/SiO_2 catalysts

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Abstract

This work aimed to convert glycerol (a by-product of biodiesel production[1]) into acrolein, a high value-added product[2], enhancing the biodiesel production chain and as an alternative to its petrochemical production from propylene[3,4]. The catalysts were synthesized using the Pechini method[5,6], containing 10 and 20% niobium dispersed in silica and calcined at 500ºC (10NbSi500 and 20NbSi500, respectively). A pure Nb_2O_5 catalyst was also synthesized for comparison. The materials were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). From the diffractograms, it was identified that for the pure Nb_2O_5 solid there was the formation of characteristic peaks concerning the TT-Nb_2O_5 phase[7] (ICDD 028-0317). The patterns of the samples containing 10 and 20% niobium show that the crystallinity of the materials depends on the Nb content dispersed in the silica matrix, with 20NbSi500 being more crystalline. The FTIR spectra showed a shoulder at 3385 cm^{-1} indicating hydroxyl moieties (Nb-OH), bands at 846 cm^{-1} and 420 cm^{-1} indicating the formation of Nb_2O_5 crystals and a band at 925 cm^{-1} indicating the formation of a Si-O-Nb binary system. The materials were applied in the catalytic glycerol dehydration of in the gas phase using a fixed bed reactor, at a temperature of 250ºC and the products were analyzed by gas chromatography (GC). The tests initially during 180 min and showed glycerol conversion of 79.28% and 96.44% and acrolein selectivity of 88.50% and 75.79% for 10NbSi500 and 20NbSi500, respectively. These results can be related to the presence of Brønsted acid sites in the materials, due to the presence of hydroxyls as demonstrated by FTIR analysis. The 20NbSi500 sample was selected for stability tests due to its superior performance during 600 min and thermogravimetric analysis (TGA) was performed for the spent catalysts. The results showed that the 20NbSi500 material has high resistance to deactivation with glycerol conversion (68.25%) and is highly selective to acrolein (71.00%) in 600 min. These results can be attributed to its excellent textural properties such as surface area (243 m^2/g), pore size (0.77 nm) and pore volume (12.95 nm) which were determined by N_2 physisorption at 77K. TGA analysis revealed a mass loss of 14%, attributed to soft coke[8], with burning at 414ºC, according to DTG. These results show that 20NbSi500 is efficient in the glycerol conversion to acrolein and has high resistance to deactivation, making it promising for industrial use. Furthermore, the same solid was performed in the presence of blonde glycerin from the biodiesel industry, reaching values similar to bi-distilled glycerin.
Keywords: Glycerol dehydration; Acrolein; Niobia; Silica; Catalytic stability

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