XIV ENCAT
Encontro de Catálise do Norte, Nordeste e Centro-Oeste
Catálise: Impulsionando a transição energética para um futuro mais sustentável
17-19 novembro 2024 • Fortaleza
SBCAT SOCIEDADE BRASILEIRA DE CATÁLISE

AREA: Synthesis and characterization of catalysts and adsorbents

Synthesis of NiAl and Mo/NiAl catalysts for the production of sustainable fuels

Maria do Carmo Marcelino[1]*, Juan Felipe González[1], Celmy B.M. Barbosa[1], José Geraldo A. Pacheco[1], Santiago Arias[1], Roger Fréty[1], Luiz Stragevitch[2], Florival R. Carvalho[2].

1 Laboratory of Refining and Clean Technologies/ Department of Chemical Engineering/ Research Institute in Petroleum and Energy/ Federal University of Pernambuco/ Recife-PE, Brazil

2 Laboratory of Fuels/ Department of Chemical Engineering/ Research Institute in Petroleum and Energy/ Federal University of Pernambuco/ Recife-PE, Brazil

**E-mail: maria.marcelino@ufpe.br*

Due to the environmental impact caused by the burning of fossil fuels, the production of biofuels from catalytic deoxygenation of vegetable oils stands out as a promising strategy for energy transition [1]. In this context, the catalyst is essential to ensure high conversion and selectivity, with emphasis on nickel (Ni) catalysts, which have high thermal and chemical stability and high hydrogenation activity, facilitating deoxygenation. Molybdenum (Mo), on the other hand, has low electronic density and high electronegativity, which increases deoxygenation efficiency and acts synergistically with Ni, enhancing its catalytic activity. The use of high aluminum (Al) content favors the formation of mixed oxides with a large surface area, basicity, and thermal stability, and allows phase segregation, improving Ni dispersion and increasing its resistance to sintering [2,3]. This work is about the synthesis and characterization of the NiAl catalyst derived from layered double hydroxides (LDH) with high aluminum content. The precursor with composition $Ni_{0,2}Al_{0,8}(OH)_2(TA)_{0,4}{\cdot}mH_2O$ was synthesized by the slow addition of metal nitrates and terephthalic acid solutions in NaOH (1M) to boiled deionized water (65 °C) under constant stirring and pH. The precipitate was kept under agitation and heating for 4 hours and then at room temperature for 18 hours. After filtration and washing, the material was dried in an oven at 100 °C overnight and calcined at 600 °C for 3 hours at a heating rate of 10 °C min^{-1}, forming the NiAl mixed oxide catalyst, which was also used as a support for the impregnation of 15% molybdenum by the wet method with an ammonium heptamolybdate solution ($(NH_4)_6Mo_7O_{24}$) and later calcined to obtain the Mo/NiAl catalyst. The materials were characterized by XRD, TGA, NH_3-TPD, H_2-TPR, FTIR, EDX, and N_2 adsorption/desorption. TGA established 500 °C as the minimum calcination temperature. X-ray diffractograms confirmed the formation of NiAl LDH and the mixed oxide (with NiO and $NiAl_2O_4$ phases) after calcination. H_2-TPR analysis confirmed the presence of molybdenum, which increased the catalyst's reducibility ($V_{TPR\text{-}NiAl}$ = 663,9 mL H_2/g e $V_{TPR\text{-}Mo/NiAl}$ = 1098 mL H_2/g). With the addition of molybdenum, the surface area and pore volume slightly decreased (S_{NiAl} = 225 m²/g, $S_{Mo/NiAl}$ = 215 m²/g, $V_{p\text{-}NiAl}$ = 0,6 cm³/g e $V_{p\text{-}Mo/NiAl}$ = 0,5 cm³/g). TPD analysis showed that the NiAl catalyst has a higher density of acidic groups (1230.9 µmol NH_3/g) compared to Mo/NiAl (709.0 µmol NH_3/g), attributed to the reduction of stronger acid sites. Therefore, the results of the analyses indicate that both NiAl and Mo/NiAl have promising characteristics for use as catalysts in catalytic deoxygenation reactions.

Keywords: Layered double hydroxides (LDH), Mixed oxides, Catalytic deoxygenation.

Referências

[1] Di Vito Nolfi, G.; Gallucci, K.; Rossi, L. Green Diesel Production by Catalytic Hydrodeoxygenation of Vegetables Oils. International Journal of Environmental Research and Public Health 2021, 18, 13041. https://www.mdpi.com/1660-4601/18/24/13041

[2] Andrew Ng Kay Lup, Faisal Abnisa, Wan Mohd Ashri Wan Daud, Mohamed Kheireddine Aroua. A review on reactivity and stability of heterogeneous metal catalysts for deoxygenation of bio-oil model compounds, Journal of Industrial and Engineering Chemistry, Volume 56, 2017, Pages 1-34, ISSN 1226-086X, https://doi.org/10.1016/j.jiec.2017.06.049.

[3] Arias, Santiago; Eon, Jean Guillaume; San Gil, Rosane A. S.; Licea, Yordy E.; Palacio, Luz Amparo; Faro, arnaldo C. Synthesis and characterization of terephthalate-intercalated NiAl layered double hydroxides with high Al content. Dalton Transactions (2003. Print) v. 42, p. 2084-2093, 2013. https://doi.org/10.1039/C2DT31502E

Agradecimentos

The authors thank to CNPq (process nº 408063/2022-0) for financial support. The first author also acknowledges the support of the ANP Human Resources Program and the PRH 30.1 from UFPE.