

EFFECT OF CaO-DOPING ON COKE FORMATION ON Ni/ZrO₂ CATALYSTS IN ETHANOL STEAM REFORMING

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Hydrogen is considered as the future energy vector and ethanol steam reforming is promising to produce hydrogen in a clean way. Nickel is known to be active in reforming reactions, although it can be quickly deactivated by coking and sintering [1]. Ni/ZrO₂ is highly active in steam reforming reactions [2, 3, 4] because of its properties, such as high surface area, high stability under the reaction conditions, strong interactions with the active phase. Nevertheless, zirconia is known to be a solid acid and the presence of acid sites on the surface of the support is related to some of the side reactions responsible for coke formation. The addition of oxides of alkaline earth metals, which are strong Lewis bases, can decrease the acidity of the support. The aim of this work is to prepare Ni/ZrO₂ catalysts modified with different amounts of CaO and to evaluate the effect of the addition of a basic oxide on the overall Lewis acidity of the support, and then on carbon balance. The catalysts were characterized in order to establish the possible effect of CaO-doping also on other physico-chemical properties.

Zr(OH)₄ was prepared by a precipitation method [2] at a constant pH of 10. Ni (8 wt%) and CaO (0, 3, 6, 9 wt%) were introduced on the support by means of co-impregnation with an aqueous solution of the corresponding precursors. Samples were calcined at 500 °C. Samples are denoted as ZCa_xNi, where Ca_x indicates the percentage of CaO. The catalysts were thoroughly characterized in order to assess the physico-chemical properties of both the support and the final catalyst. Activity tests were performed after reduction of the catalysts in H₂ flow for 1 h at 500 °C. The activity tests were carried out at atmospheric pressure by feeding a 3:1 (mol/mol) H₂O:CH₃CH₂OH mixture at 500 °C.

The results showed that CaO-doping did not affect some properties of the catalysts, such as the specific surface area of the support and Ni dispersion. All samples present small and dispersed Ni nanoparticles, that are essential in order to minimize coke formation. By contrast, CaO addition to zirconia effectively reduced the Lewis acidity of the support, involved in coke deposition, and produced oxygen vacancies, which seem to affect Ni reducibility. The progressive decrease of the Lewis acidity of the support showed beneficial in improving catalyst resistance towards coking, with sample ZCa₉Ni showing the best performance. Moreover the presence of oxygen vacancies, which can activate CO₂, seems to favour the gasification of coke.

References. [1] Zhang, Z., Verykios, X.E. (1996): *Appl. Catal. A: General*, **138**, 109-133; [2] Nichele, V., Signoretto, M., Menegazzo, F., Gallo, A., Dal Santo, V., Cruciani, G., Cerrato, G. (2012): *Appl. Catal. B: Environ.*, **111–112**, 225-232; [3] Rossetti, I., Biffi, C., Bianchi, C.L., Nichele, V., Signoretto, M., Menegazzo, F., Finocchio, E., Ramis, G., Di Michele, A. (2012): *Appl. Catal. B: Environ.*, **117–118**, 384-396; [4] Rossetti, I., Gallo, A., Dal Santo, V., Bianchi, C.L., Nichele, V., Signoretto, M., Finocchio, E., Ramis, G., Di Michele, A. (2013): *ChemCatChem.*, **5**, 294-306.