SUPPORT-INDUCED EFFECTS ON THE CO_2 HYDROGENATION PERFORMANCE OF $Ni/Ce_{1-x}Zn_xO_\delta$ CATALYSTS

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ABSTRACT

The scheme of CO_2 hydrogenation is one of the most promising pathways for both the industrial CO_2 emissions valorization and the curtailment of intermittent renewable sources, such as solar and wind [1]. This reaction inevitably requires a catalyst, with nickel and ceria being among the most studied active metals and supporting materials, respectively [2]. Also, support modification via aliovalent metal doping can induce several changes in a metal/metal oxide system, with great implications in the overall catalytic performance [3]. In this work, the effect of ZnO doping on the physicochemical properties and CO_2 hydrogenation performance over CeO_2 supported nickel-based catalysts was examined. In specific, catalysts with 8 wt.% Ni supported on either bare ZnO, CeO_2 nanorods or a mixed ZnO-CeO_2 oxide were synthesized by a modified hydrothermal method and were characterized by a variety of techniques, namely N_2 physisorption, XRD, Raman spectroscopy, SEM/EDS, TEM, H_2-TPR, CO_2-TPD and CO-TPD. Notable modifications in the reaction pathway were demonstrated, as the presence of ZnO induced an increase in CO production at $T < 450\ ^oC$, whereas Ni/CeO_2 was completely selective to methane at the same temperatures. These findings were attributed to the inhibitory effect of ZnO on the redox properties, evidenced by H_2-TPR and Raman spectroscopy, the decrease in surface basicity required for CO_2 activation, revealed by CO_2-TPD and the increasing affinity for CO desorption (evidenced by CO-TPD experiments), a possible intermediate species for CO_2 methanation [4]. On the contrary, Ni/CeO_2 was associated with augmented reducibility, higher surface area, high moderate and total surface basicity, as well as strong CO affinity, which are crucial for the attainment of remarkably high CH_4 yields.

KEYWORDS: CO_2 hydrogenation, Ni/CeO_2, ZnO promotion, Selectivity change

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