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CO₂ methanation employing Ni supported on mixed oxides.

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Nowadays, CH₄ is an energy carrier very relevant for the transport sector and industry which is employed in many countries being Brazil one of them. The production of bio-SNG (bio synthetic natural gas) from CO₂ and H₂, the latter generated from H₂O electrolysis or photochemistry is a very promising utilization of CO₂ as raw material. Sabatier and Senderens discovered CO₂ methanation in 1902. However, there is no mechanism fully accepted for Ni based catalyst when mixed oxides are employed as support. Thus, the objective of this work is to contribute to the description of this relevant reaction. Three catalysts

were prepared by Ni(NO₃)₂ impregnation on *m*-ZrO₂, Mg(Al)O and SiO₂. The Ni loading of these catalysts was tuning in order to reach the same metal surface area. The following characterization techniques were employed: TPR, TPSR, CO₂-TPD, XRD (Rietveld method), models reactions and others. The methanation of CO₂ were carried out employing a microreactor employing de following conditions: 200 mg and 80 mLmin⁻¹ of a mixture comprised of 10% of CO₂, 40%H₂ and He (balance), mass and flow rate, respectively.

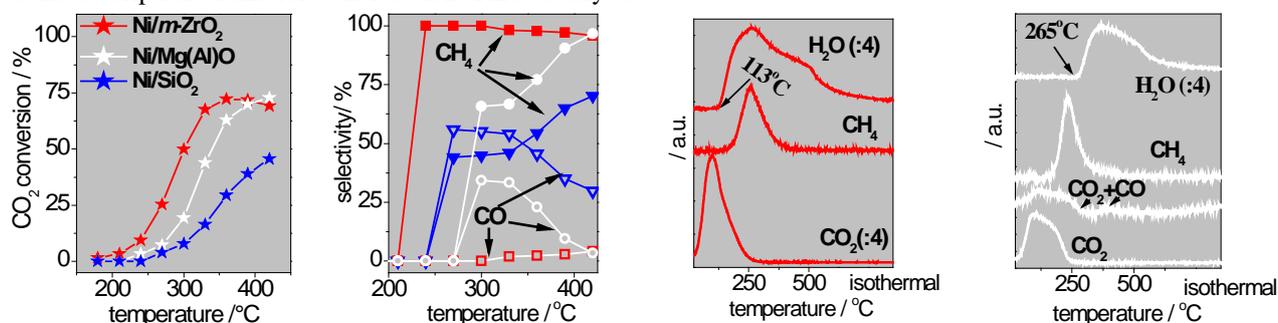


Fig. 1 conversion versus temperature, Fig. 2 selectivity versus temperature, Fig 3 TPSR spectra over Ni/ZrO₂, Fig.4 TPSR spectra over Ni/Mg(Al)O

Fig.1 shows that Ni/Mg(Al)O and Ni/*m*-ZrO₂ are much more active and selective to methane than Ni/SiO₂. As these three catalysts exhibit the same metallic area this result can be associated with the support activity. Two main mechanisms have been proposed for the CO₂ methanation on mixed oxides. The first one is related to the adsorption of CO₂ on the support followed by the carbonate hydrogenation to methane. The second one is related to the RWGS reaction (CO₂+H₂ => CO+H₂O, redox step) followed by CO methanation. The Ni/*m*-ZrO₂ XRD analysis showed that some Ni is in the lattice of *m*-ZrO₂ generating O vacancies. The Mg catalyst also exhibits O vacancies (EPR data). Moreover, *m*-ZrO₂ also shows stronger basic and acid sites than Ni/Mg(Al)O. Considering the two steps mechanism, CO₂ is reduced to CO on the O vacancies of the supports. Then, H (H₂ is dissociated on the Ni⁰) spillover from Ni⁰ to the support

and reacts with the O of the “vacancy” producing H₂O and closing the catalytic cycle. Fig. 3 and 4 show that Ni/*m*-ZrO₂ generates H₂O at much lower temperatures than Ni/Mg(Al)O. Thus, the former is easily reduced. Indeed, Ni/ZrO₂ synthesizes methane at much lower temperature than Ni/Mg(Al)O (Fig. 2). This might occur due to its higher reducibility. Moreover, the Ni/Mg(Al)O catalyst shows higher CO selectivity at temperatures higher than 300°C. This means that Ni/*m*-ZrO₂ is more active in CO methanation. The slower step of CO methanation is the C-O bond scission. As *m*-ZrO₂ shows stronger basic and acid sites than Ni/Mg(Al)O these properties might promote CO methanation. Thus, the catalytic behavior of the Ni supported on mixed oxide catalysts in the methanation reaction seems to be associate with the two steps mechanism wherein redox, acidity and basicity properties of the supports are relevant.