Dry reforming of methane comes as a great option to handle the current environmental and sustainability energetic concerns, because, as it converts two greenhouse gases, produces H_2, which is a widely known energy carrier.

Between the most used catalysts, the ones based in Ni are the most known. They have an excellent activity/price ratio but coke deposition or/and sintering of the Ni particles usually deactivates them.

One of the techniques to improve its resistance to deactivation, and even to improve its catalytic activity is their modification with a second metal like Ru.

The present work explores two different synthetic routes based on impregnation methods that lead to modified Ni catalyst that even with the same metal composition display a very different catalytic behavior, revealing that the interaction metal-metal (Ni-Ru) plays a very interesting role in the performance of this kind of catalyst.

The Ni-Ru catalysts were prepared by impregnation following two different routes. The ***Simultaneous*** route (S samples) (C samples): Alcoholic solutions of $Ni(NO_3)_2.6H_2O$ and $Ru(NO)(NO_3)_3$ are mixed and then impregnated on the modified alumina support. After impregnation, the catalyst was dried at 120ºC overnight and finally calcined in air at 500ºC/5 h. The ***Consecutive*** route: The modified alumina support is first impregnated with an alcoholic solution of $Ni(NO_3)_2.6H_2O$, dried ovenigth at 120ºC and calcined in air at 500ºC for 5h. Afterwards, the alcoholic solution of $Ru(NO)(NO_3)_3$ was impregnated. Finally, the catalyst is dried and calcined as previously described. The nominal values of Ru are 0,5 and 2%, the Ni content is always 15%. The catalytic tests were carried out in a fixed bed quartz reactor using a feed mixture of $CH_4/CO_2/N_2$ 35/35/30 working at 110 $L \cdot h^{-1} \cdot g^{-1}$. The reforming tests were performed at 750 °C for10h.

The extent of incorporation of Ni and Ru was similar in both routes and the desired values of metal phase were achieved.

The addition of Ni barely changes the textural properties of the modified alumina used as support, and the addition of Ru doesn't have any influence in the textural properties. All solids present a Type IV isotherm, which is typical for mesoporous solids, with a H1 hysteresis, which indicates a cylindrical-interconnected type of pores.

The XRD patterns of all solids are dominated by those peaks of the support, characteristics of a Mg and Al spinel ($MgAl_2O_4$). In all samples Ni is detected as NiO, and Ru as RuO_2, except in the S_0,5Ru sample, where no RuO_2 peaks are detected. This could be owed to a better dispersion of RuO_2, or to the formation of a mixed-oxide Ni-Ru, or even to a possible inclusion of Ru^{+4} in the support network. This result suggests a stronger Ni-Ru interaction in the samples prepared by the simultaneous route, preferably at lower ruthenium contents.

The existence of such Ni-Ru interaction is highlighted by Raman spectroscopy. The Raman spectra of the samples synthesized by the consecutive route show typical RuO_2 bulk vibrations, while a Raman spectrum characteristics of low-dimensional RuO_x species is presented for the ones synthesized by the simultaneous route.

An *in situ* XRD study in presence of H_2 was performed over both series of catalysts (Figure 1). As the temperature increases, all Ru samples, except S_0,5Ru, present a clear diffraction peak at 44º 2θ, which correspond to the [101] plane of Ru^0. Again, the no appearance of the metallic ruthenium diffraction peaks could be indicative of a singular interaction between Ru and Ni or to a smaller particle Ru size owed to a better dispersion.

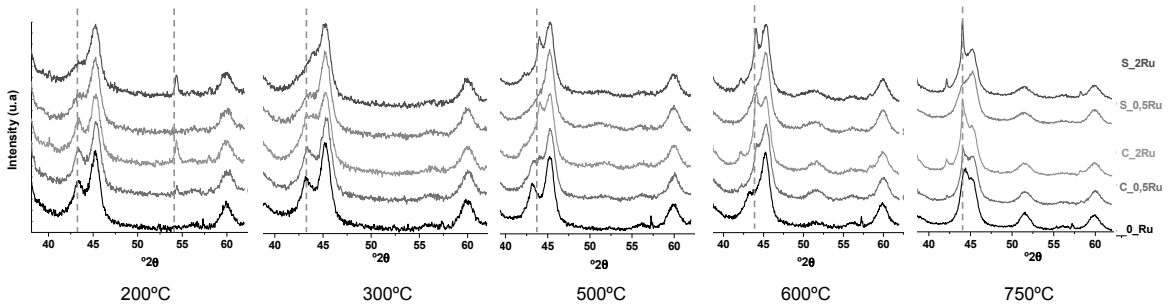
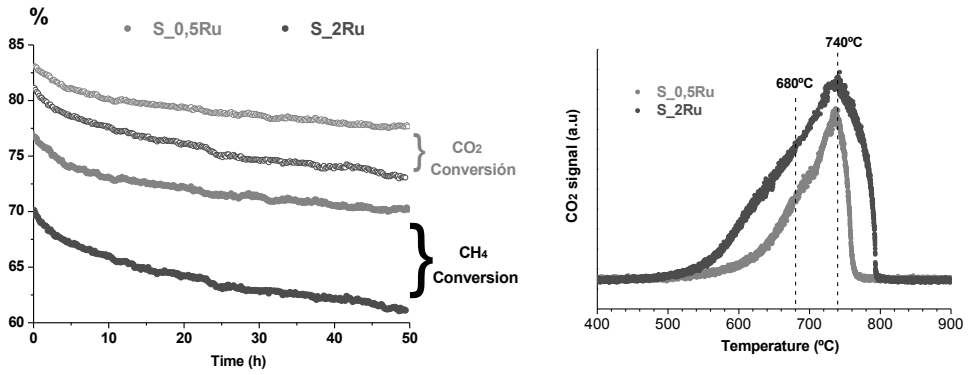


Figure1. XRD in reductive conditions.

Finally, the stronger Ni-Ru interaction in the samples synthesized by the Simultaneous route is confirmed by the TPR analysis. Although all Ru modified samples present a better and easier reducibility of the Ni species, shifting the nickel reduction processes to lower temperatures, a higher percentage of reducibility is obtained over the samples prepared by the simultaneous route. Besides this, a new reduction process at low temperatures (<220ºC) due to the ruthenium reduction is detected in all samples, such process (temperature, H_2 consumption and profile) differing for both series indicating the different ruthenium-nickel contact.

Concerning the catalytic activity, those samples prepared by the simultaneous route present higher CH_4 and CO_2 conversion values than those of the consecutive one. Besides this, the S-0,5Ru sample has the best catalytic results, despite the lower amount of Ru. The stability test carried out over these two samples during 50 hours also evidences the lower deactivation rate showed by the S-0,5Ru catalyst, which agrees with its lower amount of coke determined over the reacted sample by TPO and Raman studies (Figure 2).



A. B.

Figure 2. A. CH_4 and CO_2 conversions during 50h. B. TPO of the post reaction samples.

Compared to the consecutive impregnation procedure, the simultaneous impregnation of Ru and Ni over a modified alumina support leads to catalysts with a higher Ru-Ni interaction, specially at low ruthenium content, resulting in more active and resistant to coke deactivation catalyst for the dry reforming of methane.