

RESPONSE TO REVIEWERS

Manuscript title: Effect of metal dopant on the performance of Ni@CeMeO₂ em-bedded catalysts (Me = Gd, Sm and Zr) for dry reforming of methane.

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The authors would like to thank the reviewers for the time dedicated to critically review the manuscript and their relevant comments and suggestions. Addressing all the concerns helped us to improve the quality of the document.

Below we respond all the issues highlighted by the reviewers and we also indicate the changes carried out within the manuscript.

Reviewer#1

The manuscript fits well with the scope of the journal and the results are well presented. I suggest only small improvements.

For the DRM test, the Thermodynamic has to be presented in order to show the potential of such materials. Also I suggest to the authors to comment a bit more the following part

"The CO₂ conversion is higher than CH₄ conversion for all catalysts while the H₂/CO molar ratio is lower than 1.0. These results suggest the occurrence of the reverse water-gas shift (RWGS) reaction, which is thermodynamically favored at the reaction conditions used. Similar result was reported by other authors [30,40,53]."

Reply: The authors agree with the reviewer and a thermodynamic analysis was added associated to the Fig. 7. This analysis was performed assuming no carbon formation by using Gibbs free energy minimization algorithm on Aspen HYSYS Software. The potential of the materials were analyzed by comparison with the TOF values obtained in the literature for Ni/MgO reference. The catalysts presented similar activity.

In terms of deactivation analysis, the stability tests must be performed far from thermodynamic conversion to avoid an excess of catalyst and a misinterpretation in the calculation of the carbon formation rate. Furthermore, the reverse water gas shift (RWGS) reaction is an endothermic reaction thermodynamically favored at high temperature, converting the CO₂ in CO in the presence H₂. It is a highly reported side reaction in reforming process responsible to decrease the H₂/CO molar ratio in the syngas produced. The following text and Fig. 7 were added in the pages 11-12:

"Fig. 7 displays the conversions of CO₂ and CH₄ expected at the thermodynamic equilibrium as a function of temperature. This analysis was performed by using Gibbs free energy minimization algorithm on Aspen HYSYS Software assuming no carbon formation. At 800°C the conversions of 95 and 90% are reached at the equilibrium for CO₂ and CH₄ respectively. The highest conversion for CO₂ is explained by the occurrence of the reverse water-gas shift reaction (RWGS : CO₂ + H₂ → CO + H₂O) which is an endothermic reaction thermodynamically favored at high temperature, converting the CO₂ in CO in the presence H₂. This side reaction leads to a decrease of the H₂/CO molar ratio in the produced syngas".

...

“The stability test was carried out to evaluate the resistance of the catalysts to carbon deposition during the DRM. The operating conditions were adapted in order to avoid reaching the thermodynamic equilibrium, allowing a relevant comparison in terms of catalyst deactivation.”

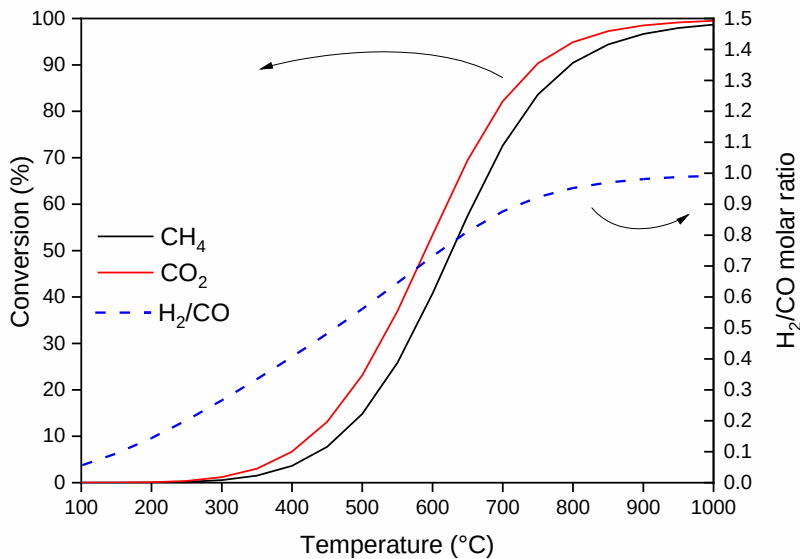


Figure 7. Thermodynamic conversion and H₂/CO molar ratio assuming no carbon formation in the DRM reaction.

Finally, it would be good, also in the catalytic part to show the impact of each promoting element in the CeOx support and link it with catalytic activity

Reply: It is generally agreed that the dissociation of methane on the catalyst is the rate determining step and it occurs over the Ni surface. Therefore, since there is not a highly pronounced change in the Ni dispersion, it is expected that the catalyst activity does not change in function of the ceria dopant. The dopant plays a key role only in the deactivation process to increase the Ni resistance to sintering and the oxygen mobility in the support.