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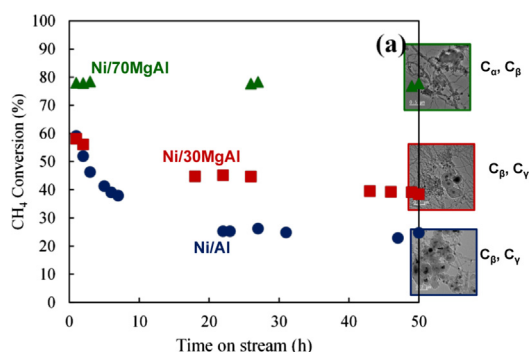
Upgrading greenhouse gases (methane and carbon dioxide) into syngas using nickel-based catalysts



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GRAPHICAL ABSTRACT



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ABSTRACT

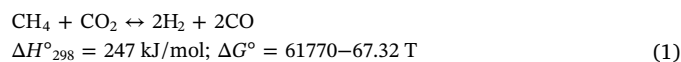
In this work, Mg-doped Al₂O₃ supports were used for the preparation of Ni catalysts, which were then tested in dry reforming of methane reaction (DRM) for syngas production. The influence of MgO content (0–70 wt%) on the basicity of the catalysts as well as on the formation of a NiO-MgO solid solution was investigated and linked to the catalytic performance of the catalysts. The catalyst containing high amount of Mg (Ni/70MgAl) showed the best performance with negligible deactivation rate over 50 h of time on stream (TOS). The presence of strong basic sites in this catalyst was important to adsorb carbon dioxide (CO₂), to gasify the coke deposit and to increase the syngas production. Also, the presence of a NiO-MgO solid solution led to strong metal-support interaction, which limited the sintering of nickel particles. The quantification of the water formed during the reaction showed that its formation was crucial for the elimination of the coke deposits as well as to increase the syngas production.

1. Introduction

CO₂ reforming of methane, also known as dry reforming of methane, (Eq. (1)) has received great attention in the past few years since it converts CO₂ and CH₄, the two main greenhouse gases, into syngas, which can be later used for the production of energy, fuels and added-

value chemicals, such as dimethyl ether, formaldehyde, olefins, etc [1,2].

Dry reforming of methane (DRM):



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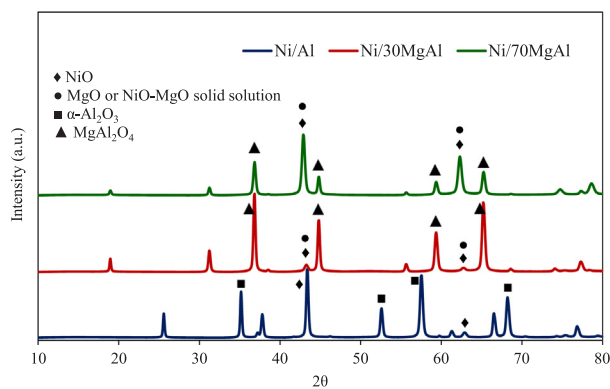


Fig. 1. XRD patterns of the fresh catalysts.

Table 1
XRD characterization of the 70MgAl support and Ni/70MgAl catalyst.

Sample	MgO or solid solution XRD parameters			Possible match	MgO (wt%)	R _{Bragg} ***
	2θ	Cell a = b = c (Å)	d [†] (nm)			
70MgAl	42.88	4.214	12.8	MgO	59.7	1.81
Ni/70MgAl	42.86	4.212	16.9	MgO or solid solution	66.2**	1.88

* Crystallite size calculated using the Scherrer equation.

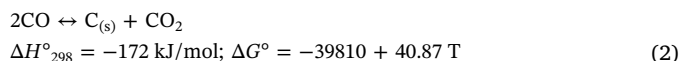
** Considering that the peak at 42.86° correspond only to MgO.

*** From Rietveld refinement.

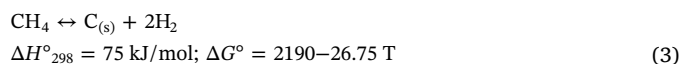
Despite the economic and environmental benefits of this process, there is not yet a DRM full scale plant operation up to date [3]. The main reasons are the high energy requirements of the reaction and the fast deactivation of the catalysts due to coke deposition and sintering of both support and active phase at high reaction temperatures.

So, much effort has been done to develop thermally stable catalysts with good performance for this process. Supported noble metal (Ru, Pd, Pt and Rh) catalysts proved to have good catalytically performance. However, their high cost and limited availability are significant drawbacks [4–6]. So, transition metals, especially Ni, have been widely studied due to their lower cost and higher accessibility compared to noble metals and proven activity in this process [7]. Nevertheless, they were reported to be more prone to carbon deposition on the catalyst surface (Eqs. (2) and (3)) and present low resistance against the sintering of the active phase, which considerably reduce their stability [1,8–10].

Boudouard reaction:



Methane cracking reaction:

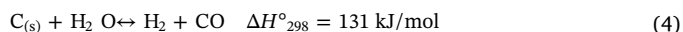


So, there has been many studies to improve the coke resistance of the Ni-based catalysts. One possible pathway is the addition of alkali promoters, which increase the basicity of the support and favors the CO₂ adsorption which will further oxidize the carbon deposit [11–15]. According to Ballarini et al. [14], these promoters may act as texture, structure and activity promoters, enhancing the thermal stability of the alumina-based supports and preventing sintering of the support and of the active phase. They would also improve the metal dispersion and the ability of the catalyst to gasify the coke deposit. San Jose-Alonso et al. [16] investigated the influence of potassium (K) over the performance of the Co/Al₂O₃ catalyst. Promoted catalyst showed lower coke deposition compared to unpromoted catalyst. This was explained by a partial coverage of the active sites for the methane decomposition by K addition and its ability to catalyze the carbon gasification reaction.

Several works have demonstrated that the formation of a NiO-MgO solid solution could also hinder the deactivation by coke deposition. Bradford and Vannice [11] showed that the formation of NiO-MgO solid solution could stabilize the Ni particles, which prevented carbon deposition over Ni/MgO catalyst in DRM reaction. Hou et al. [17] added that the combination between NiO and MgO results in a very stable solid solution with a basic character, which is efficient in inhibiting the coke deposit.

Addition of water to the feed has also been used to inhibit carbon formation via a carbon gasification reaction (Eq. (4)) [11].

Carbon gasification:



Rostrup-Nielsen [18] showed that the coke could be gasified by different gases such as hydrogen, carbon dioxide and steam. However, steam would be the most effective one. Similar conclusions were obtained by Figueiredo et al. [19]. They showed that the rate of coke gasification with hydrogen is considerably slower than with steam.

In the present work, Ni supported on Mg-doped Al₂O₃ catalysts, with different amounts of MgO, were tested in the DRM reaction. The aim was to understand the influence of the catalysts basicity (linked to the amount of Mg) on the catalyst activity and stability, and the role of the water formed during the reaction. The novelty of this work is the successful combination of different methods for structural characterization of catalysts before and after catalytic test to understand the deactivation mechanism and the impact on the conversion of CO₂ and CH₄ into syngas. The water formed during the reaction could be experimentally quantified and linked to the catalytic performance of catalysts synthesized in this work. This contributes to the basic understanding of DRM process and to the design of an efficient catalyst for DRM.

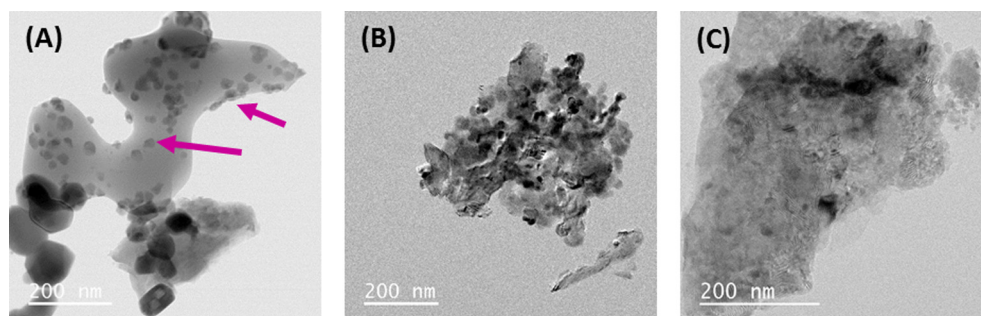


Fig. 2. TEM of fresh catalysts: (a) Ni/Al, (b) Ni/30MgAl and (c) Ni/70MgAl; → pink arrow: nickel particle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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