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Syngas production from dry reforming of methane over ni/perlite catalysts: Effect of zirconia and ceria impregnation

Farah Mesrar^a, Mohamed Kacimi^{a,**}, Leonarda F. Liotta^{b,*}, F. Puleo^b, Mahfoud Ziyad^{a,c}

^a Université Mohammed V, Faculté des Sciences, Département de Chimie, Laboratoire de Physico-chimie des Matériaux et Catalyse, B.P. 1014, Rabat, Morocco

^b Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, Palermo, Italy

^c Hassan II Academy of Science and Technology, Rabat, Morocco

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ABSTRACT

Ni catalysts with nominal loadings ranging between 2.5 and 20 wt% were synthesized over perlite by wet impregnation, then filtered, washed and calcined at 500 °C. Chemical analyses performed by MP-AES revealed that the maximum Ni content loaded over perlite corresponded to ~15 wt%. Therefore, for comparison reasons, a Ni(20 wt%)/perlite catalyst was prepared by wetness impregnation without performing any washing treatment. The so prepared catalysts were tested in methane dry reforming without performing any pre-treatment reduction. The catalytic performances were compared by increasing the temperature from 500 up to 800 °C under the reaction mixture composed of 15 vol% CH₄ + 15 vol% CO₂/N₂. Ni(15 wt%)/perlite was the most active catalyst among the series of monometallic samples. The effect of co-impregnating perlite with Ni and Zr or Ni and Ce precursors in order to obtain catalysts with final composition, Ni(15 wt%), 10 and 20 wt% as Zr or Ce, perlite (75 or 65 wt%) was, then, investigated. Characterizations performed by XRD, BET, DRS and H₂-TPR evidenced that the physico-chemical and reduction properties are influenced by the Ni content and by the presence of zirconia and ceria oxides. It is worth of noting the increased reducibility of NiO species promoted by zirconia and ceria addition. The catalytic activity in the dry reforming of methane was also affected by the presence of doping oxides, in terms of enhanced CH₄ and CO₂ conversions and higher H₂/CO atomic ratios. Runs tests at 700 °C for 12 h were carried out and the spent catalysts were analysed by TGA and TEM. Over Ni(15 wt%)/perlite large amount of amorphous carbon grows on the surface blocking the active centres, while zirconia and ceria doping improved the resistance to carbon poisoning favouring growing of filamentous carbon residues in small amount.

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* Corresponding author.

** Corresponding author.

E-mail addresses: kacimimohammed@fsr.ac.ma (M. Kacimi), leonarda.liotta@ismn.cnr.it (L.F. Liotta).

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Introduction

Until now natural gas remains the best energetic compromise compared to the other sources of non-renewable energy and fulfils the today's financial requirements, being its reserves abundant and geographically well distributed in the world.

Independently of the usage of natural gas, the approach to its rational valorisation requires search for efficient processes of production, transport, conversion and storage. Natural gas is widely used to manufacture ammonia, propanal, methanol and dimethyl ether via the syngas (CO/H₂) [1–5]. It can be used also to produce hydrogen by steam reforming of hydrocarbons [6].

The major concern of the policy-makers today is the increase of greenhouse gases, which cause the acidification of the oceans and other disastrous phenomena, especially the earth global warming [7]. These climatic changes can be attenuated if the CO₂ concentration in the atmosphere would be reduced to low ppm values. On the other hand, it must be kept in mind that many natural gas reserves contain large quantities of CO₂. Such supplies might be valorised if they are converted into high-value-added products and hydrogen [8].

Methane dry reforming (DRM) (CH₄ + CO₂ ↔ 2CO + 2H₂) is among the reactions that attracted most the attention of researchers in the last years [9]. The reaction is highly endothermic ($\Delta H^{\circ}_{298K} = +247 \text{ kJ mol}^{-1}$) and normally requires temperatures above 700 °C in order to reach desirable conversion levels. The composition of the produced syngas approaches a ratio H₂/CO near 1, when a high selectivity towards CO₂ reforming of methane is achieved.

The H₂/CO ratios produced from CO₂ reforming of methane is a function of the temperature and CO₂/CH₄ ratio and the desirable value varies with different industrial applications, such as synthesis of oxo-alcohols, acetic acid, dimethyl ether, C₂ hydrocarbons [10,11].

According to detailed theoretical thermodynamic calculation the DRM is thermodynamically favoured at temperatures higher than 700 °C [11], therefore the development of efficient catalysts active and selectivity towards syngas production at T ≥ 700 °C is highly required [12–14]. Despite their high cost, noble metals based catalysts are resistant to carbon deposits and appropriate for industrial usage [15]. Among transition metals, nickel remains the most studied for methane dry reforming because of his good activity and selectivity to H₂ despite the poisoning by carbon deposits [15–21]. Improvement of Ni catalysts can be achieved by modifying with additives such as alkalis, rare earth compounds and noble metal promoters, which reduce carbon deposits [20,22–26].

The deactivation of Ni catalysts can be induced also by other factors such as the sintering of the active particles. The beneficial action of additives is principally attributed to their dispersive effect, basic and redox properties [27–30]. It is shown that the mixed oxide supports CeO₂-ZrO₂, CeO₂-Al₂O₃, and La₂O₃-Al₂O₃, prepared using surfactant, exhibit a high catalytic activity and stability for DRM [30].

Some of us have recently reported that small amount of noble metals, such as Au and Pt, can affect the type of carbon formation, inhibiting the poisoning by coke deposition and at the same time, stabilize Ni against sintering through alloy

formation [31,32]. Moreover, the doping Al₂O₃ with CeO₂ (10 wt %) significantly improved the catalytic performance of the Ni (4 wt%) catalyst and lowered the amount of carbon deposits [32].

Natural oxides such as clays, phosphates and volcanic rocks (namely, pumice, perlite or vermiculite) have great abundance, therefore, low price and show beneficial properties for their morphology and chemical composition, thanks to the presence of basic oxides that usually are added to the catalysts formulations [33].

Perlite is an amorphous volcanic glass which contains approximately 70–75% of SiO₂, 12–18% of Al₂O₃ along with some alkali and alkaline earth metal oxides. Perlite has several advantages such as high porosity with strong adsorbability, excellent thermal and chemical resistance, light weight, low cost, low toxicity and ease of handling. The use of perlite has been reported for the immobilization of TiO₂ for photocatalytic applications, such as decomposition of phenol and ammonia [34,35]. Perlite granules as support have porosity of more than 95% and density of 64–144 kg/m³ that allows them to stay afloat on water surface [35]. On the other hand, only a few reports concern the use of perlite as support for heterogeneous catalysts. Recently, perlite has been used as a support for the immobilization of copper nanoparticles for reduction of 4-nitrophenol in water [36]. Moreover, perlite has been successfully applied as support for immobilization of sulfonic acid as a heterogeneous solid acid catalyst for the heterocyclic multicomponent reaction and as well for one-pot three component synthesis of 1,2-dihydro-1-aryl-naphtho [1,2-e] [1,3]oxazine-3-one [37,38].

However as far as we know, there are no reports of using of perlite as a support for the preparation of Ni-based catalysts for dry reforming of methane.

We have recently reported that Ni deposited over apatite-like oxide prepared by dissolution-precipitation of natural phosphate is an effective catalyst for dry-reforming of CH₄, showing high catalytic activity at 700 °C and good stability in hydrogen yield, suggesting great resistance to coke poisoning according with the basic nature of the support [39].

Based on our previous promising results and on the above mentioned application of perlite, the present work was devoted to the synthesis, characterization and investigation of Ni at different loadings over perlite, as catalysts for dry reforming of CH₄. The effect of co-impregnating perlite with Ni and Zr or Ni and Ce precursors in order to obtain catalysts with final composition, Ni15 wt%, 10 and 20 wt% as Zr or Ce, perlite (75 or 65 wt%) was addressed. Structural analysis of the spent catalysts was performed after long run tests at 700 °C for 12 h. Special attention was paid to the investigation of the different catalytic activity and selectivity to syngas, as a function of the catalyst composition.

Experimental

Catalysts preparation

The perlite used as the catalyst carrier was acquired from Perlite In. Morocco, its chemical composition, determined by microwave plasma atomic emission spectroscopy (MP-AES)

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