



Novel nickel promoted illite clay based catalyst for autothermal dry reforming of methane



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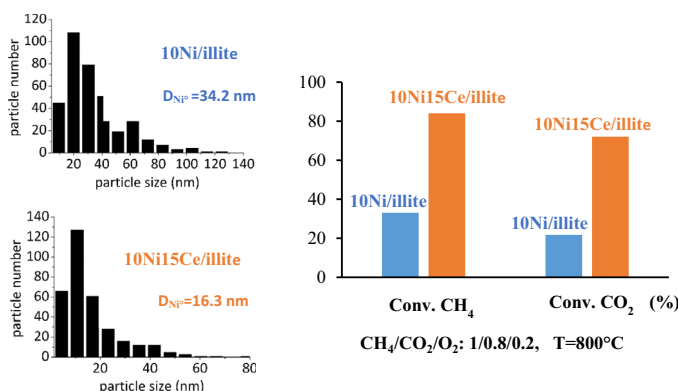
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HIGHLIGHTS

- Illite natural clay is an interesting support for the autothermal reforming of CH₄.
- The addition of Ce increases the surface area and the dispersion of nickel particles.
- The best catalytic activity and stability are obtained with the catalyst containing 15% in weight of Ce.
- High CH₄ and CO₂ conversions are maintain during 4 h on stream in the presence of O₂.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of Ni–Ce catalysts supported on illite clay containing different cerium loading were tested with respect to autothermal reforming of methane at 800 °C using a GHSV = 60,000 mL g⁻¹ h⁻¹. The addition of oxygen in the gaseous reactant feed, under the used experimental condition was found to play a key role since the carbon balance is significantly higher as compared to CH₄/CO₂ mixture.

The addition of cerium was found to enhance the specific surface area as result of meso-porosity development. Furthermore, the nickel particles become smaller in the presence of Ce, decreasing the Ni⁰ average size from 34.2 for 10Ni to 16.3 nm for 10Ni15Ce. The best catalytic activity and stability were obtained on the catalyst containing 15 wt.% of cerium, apparently attributed to its redox properties and further improvement on the nickel dispersion. It should be pointed out that the observed catalytic performance was high even after 24 h under reaction stream.

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1. Introduction

Dry reforming of methane to produce syngas is an important process for valorization of two significant greenhouse contributors.

Moreover, the reaction produces syngas with low H₂/CO ratio suitable for the production of methanol and liquid hydrocarbons using Fischer–Tropsch processes [1,2]. The reaction is known to involve active catalysts based on supported noble metals [3–5] and group 8–10 metals such as Fe, Co and Ni [6–8]. For industrial application, nickel is the metal of choice due to its inherent availability and low cost as compared to noble metals. The major drawback for nickel

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based catalysts is carbon deposition during the reaction leading to catalyst deactivation. Nevertheless, coking phenomenon was found to be limited in case of highly dispersed metal species at the surface of the support [1]. The latter is known to play an important role in the catalytic performances, particularly in terms of thermal stability considering the temperatures higher than 750 °C required for the reaction. This is the main reason for deactivation of support materials like Al_2O_3 , SiO_2 , TiO_2 , MgO , ZrO_2 ... although their higher initial activities [9]. Thus, the addition of basic and/or redox promoters was reported to decrease the formation of coke, as evidenced by Jeong et al. for alkaline metals such as Mg, Mn, K or Ca [10]. The improved catalytic activity was attributed to the partial coverage of nickel particles by metal oxide that limits carbon deposition. Of interest, the use of Lanthanides was reported to undergoes beneficial effect with respect to catalytic stability due to the presence of La_2O_3 and the formation of oxycarbonate species that act as dynamic oxygen pool facilitating coke removal [11,12]. Additionally, the presence of cerium at the support surface was reported to promote the catalytic activity due to the oxygen storage capacity of CeO_2 [13,14]. On the other hand the nickel particles size was reported to be influenced for various Ce-promoted catalysts such as $\text{Ni}/\text{Al}_2\text{O}_3$ [15], Ni/SiO_2 [16] and Ni/ZrO_2 [17]. Although, Daza et al. [18] showed that the presence of Ce does not affect the nickel particles size of mesoporous Ni-Ce/clay catalysts, apparently, because of the strongest NiO interactions with the support as compared to the one involves in NiO-CeO₂.

The use of clays emerged as interesting catalytic supports considering their great availability, low cost and specific physico-chemical properties for the dry reforming of methane, such as hydrotalcites promoted with cerium, relatively active and stable at around 550 °C as shown by Debek et al. [19]. At 700 °C improved catalytic performances were obtained with doped Ni-Mg-Al mixed oxide with $[\text{Ce}(\text{EDTA})]^-$ [20]. Hence, the use of natural clays as catalytic support was reported to be of interest regarding various possibilities of modification of their inter-lamellar space. Further incorporation of alumina species into the inter-lamellar spaces of smectite permit higher thermal stability that avoid its collapse during the calcination step [21].

Illite is among the abundant phases encountered in natural clays as result of the transformation of smectite during diagenesis and metamorphism [22]. This phase is known as interlayer-deficient dioctahedral minerals belonging to mica group with general formula: $(\text{K}, \text{Ca}, \text{Mg}) (\text{Al}, \text{Mg}, \text{Fe})_2 (\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$ [23] where potassium is commonly localized in interlayer sites and

Table 1
Chemical composition of the illite clay (wt.%).

	SiO_2	Al_2O_3	MgO	Fe_2O_3	K_2O	CaO	TiO_2
wt.%	54.4	26.6	2.1	7.6	5.8	0.4	1.4

Table 2
Designation and elemental composition of catalysts.

Designation	Ni (wt.%)		Ce (wt.%)	
	T^a	M^b	T^a	M^b
10Ni	10	10.2	0	–
10Ni5Ce	10	9.5	5	4.3
10Ni10Ce	10	10.1	10	10.0
10Ni15Ce	10	10.2	15	13.4
10Ni20Ce	10	10.0	20	18.5

^a T : Target value.

^b M : measured value.

reported to give an overall basal spacing of 1.0 nm [24]. Note that up to now, illite containing clays were mainly used as low-cost adsorbents for industrial waste treatment and not as catalyst support [25].

The aim of the present study was to study the catalytic performances of illite-based materials with respect to the dry reforming of methane, which, to the best of our knowledge has never been reported before. The investigated catalysts were prepared using a simple impregnation method of nitrate precursors. A particular interest was paid to the influence of cerium addition to the support for fixed amount of nickel at 10% in weight. Moreover the paper highlights the interest of coupling carbon dioxide reforming and partial oxidation of methane to syngas following the operating conditions optimized according to thermodynamic analysis carried out by Amin and Yaw [26].

2. Experimental

2.1. Catalysts preparation

The starting material was a natural morocco clay from the area of Tanger. Illite was separated from the raw clay by wet sedimentation according to the method based on Stokes law allowing the removal of heavier particles such as quartz. The raw clay was

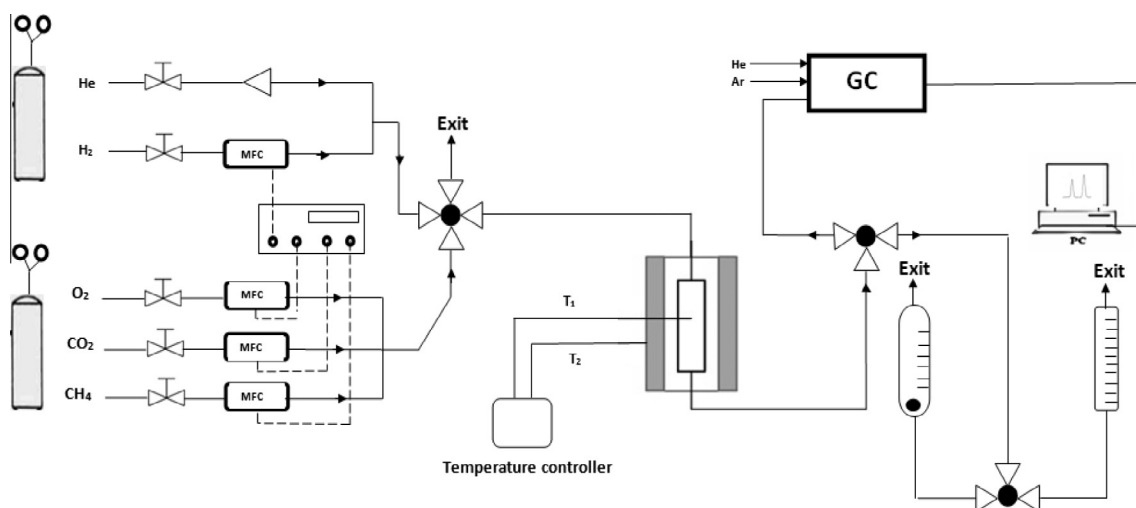


Fig. 1. Experimental setup.

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