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## Dry reforming of methane on nickel-chrome, nickel-cobalt and nickel-manganese catalysts

Karima Rouibah <sup>a,b</sup>, Akila Barama <sup>a,\*</sup>, Rafik Benrabaa <sup>a,c</sup>,  
Jesus Guerrero-Caballero <sup>d</sup>, Tanushree Kane <sup>d</sup>, Rose-Noëlle Vannier <sup>d</sup>,  
Annick Rubbens <sup>d</sup>, Axel Löfberg <sup>d,\*</sup>

<sup>a</sup> Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, Faculté de Chimie, USTHB, BP32, El-Alia, 16111 Bab Ezzouar, Alger, Algeria

<sup>b</sup> Université Mohamed Seddik Ben Yahia-Jijel, Faculté des Sciences et de la Technologie, BP 98, Ouled Aissa, 18000 Jijel, Alger, Algeria

<sup>c</sup> Université 20 Août-Skikda, Faculté de Technologie, Département de Pétrochimie & Génie des Procédés, BP 26, route Al-Hadaiek, 21000 Skikda, Alger, Algeria

<sup>d</sup> Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

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### ABSTRACT

Dry reforming of methane was investigated over Ni-based catalysts containing Cr, Mn and Co metals. The materials were synthesized via co-precipitation method and they were calcined at 800 °C in order to obtain the spinel structure NiM<sub>2</sub>O<sub>4</sub>. The structural and textural properties were characterized using: XRD, Raman and XPS spectroscopies, BET and SEM-EDX techniques. The reducibility was studied by TPR and HT-XRD techniques under H<sub>2</sub> atmosphere. The spinel structure NiM<sub>2</sub>O<sub>4</sub> was confirmed for Ni-Cr and Ni-Mn catalysts by XRD and Raman spectroscopy. In the case of Ni-Co, the results revealed the presence of cobalt oxide Co<sub>3</sub>O<sub>4</sub> with spinel structure and NiO; the NiCo<sub>2</sub>O<sub>4</sub> spinel was not observed. All catalysts were very active in dry reforming of methane with a good H<sub>2</sub> selectivity. The best catalytic performance was observed for Ni-Cr system with high CH<sub>4</sub> and CO<sub>2</sub> conversions (up to 90%), high H<sub>2</sub> selectivity (reaching 99%) and with low coke formation (4% of converted CH<sub>4</sub>).

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### Introduction

Dry reforming of methane is a process which receives an increasing interest as it contributes to reduce emission of two greenhouse gases CH<sub>4</sub> and CO<sub>2</sub> while converting them into valuable feedstock (CO/H<sub>2</sub> = 1/1) which is suitable for further

use in the Fischer-Tropsch process to produce hydrocarbons and oxygenates [1,2]. Dry reforming of methane is also an interesting way for use of biogas, a renewable resource containing CH<sub>4</sub> (40–70%) and CO<sub>2</sub> (30–60%) produced by anaerobic digestion of biomass [1,3]. In addition, due to its highly endothermic characteristic, this reaction can be applied for

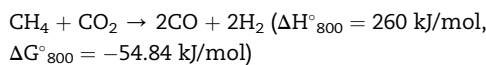
\* Corresponding authors.

E-mail addresses: [abarama@usthb.dz](mailto:abarama@usthb.dz) (A. Barama), [axel.lofberg@univ-lille1.fr](mailto:axel.lofberg@univ-lille1.fr) (A. Löfberg).

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chemical energy transmission systems as a means for storing energy provided by intermittent sources in the form of hydrogen or fuels [4].



Both noble metals (Ru, Rh, Pt, etc) and group VIII B metals (Fe, Co, Ni) are active elements in DRM catalysts [5]. Although noble metals exhibit high catalytic performances, the use of these metals remains limited due to their high cost. Thereby, transition metals are often favored. Among these metals, nickel remains the most investigated catalyst in the dry reforming of methane because of its comparable activity to that of noble metals, availability and low price [6,7]. However, although Ni-based catalysts showed high activity for DRM, they tend to deactivate due to coke formation [6,8]. Therefore, many studies have been undertaken to synthesize Ni-based catalysts with high catalytic performances to syngas production and a high resistance to carbon deposition [9]. Several studies have been proposed to limit the formation of coke. Recently, the use of oxide compounds with a spinel structure attracts increasing attention in order to obtain small active Ni particles in strong interaction with the support in order to limit deactivation of the catalysts by both sintering and coking. In previous study, Benrabaa et al. tested nickel ferrite spinel  $\text{NiFe}_2\text{O}_4$  in the DRM reaction [10]. The catalysts were prepared by co-precipitation, hydrothermal method and sol-gel process. The results showed that the method of preparation strongly influenced the reactivity of catalyst, on one hand, and on the other hand, that  $\text{NiFe}_2\text{O}_4$  catalysts without pre-treatment exhibit low catalytic performances compared to efficient catalysts in the literature. After a pre-reduction, better catalytic performances were observed only for the sample prepared by sol-gel method.

In this context, the purpose of the present work was to prepare efficient spinel catalyst  $\text{NiM}_2\text{O}_4$  for dry reforming of methane to syngas production with  $M = \text{Cr}, \text{Mn}$  and  $\text{Co}$  and to elucidate the role of the M element on the activity of catalysts and coke formation. The catalysts were prepared by co-precipitation and characterized using several techniques in order to study their structural, textural and reducibility properties before being tested for dry reforming of methane.

## Experimental

### Preparation of catalysts

The catalysts were prepared by co-precipitation using NaOH as a precipitant agent as previously described [10]. The syntheses were carried out by addition of NaOH (2 M), up to pH ~ 10, to an aqueous solution of Ni, Co, Cr or Mn nitrates. The obtained precipitates were washed by distilled water for several times, dried at 80 °C for 12 h and then calcined in air flow during 4 h at 800 °C. Samples are noted as Ni-Cr, Ni-Co and Ni-Mn.

### Characterization techniques

After calcination, X-ray powder diffraction (XRD) was performed using a Bruker AXS D8 Advance diffractometer working in Bragg-Brentano geometry using Cu  $K_\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), equipped with LynxEye detector. Patterns were collected at room temperature, in the  $2\theta = 10\text{--}90^\circ$  range, with a  $0.02^\circ$  step and 96s counting time per step. Phase identification and semi-quantitative analysis were carried out using the search/match module of the EVA software based on the RIR (Reference Intensity Ratio) values. Full pattern matching was carried out using the Fullprof suite to derive unit cell parameters and crystallite sizes. The Thompson-Cox-Hastings pseudo-Voigt function was chosen for describing the peak profiles.  $\text{LaB}_6$  was used as a standard to derive the instrument resolution.

The reducibility behavior of the samples was studied by *in-situ* XRD under hydrogen atmosphere (3%  $\text{H}_2$  in  $\text{N}_2$ , 5 L/h) ( $\text{H}_2$ -HT-XRD) at variable temperatures up to 800 °C carried out on the same type of apparatus equipped with a XRK 900 chamber and a LynxEye detector. A diffractogram was collected every 25 °C, using a 0.1 °C/s heating rate, the counting time being chosen to collect a diagram in 15 min in the  $10\text{--}90^\circ$   $2\theta$  range. The sample was displayed on a platinum sheet. After measurement, the sample was cooled down to room temperature at a 0.3 °C/s cooling rate.

The reducibility of samples was also studied by temperature programmed reduction by hydrogen ( $\text{H}_2$ -TPR), which was carried out on Micromeritics-Autochem II 2920 with a TCD detector to monitor the  $\text{H}_2$  consumption. After calibration of  $\text{H}_2$  on the TCD, the sample was placed in a U-shaped quartz reactor and pre-treated in argon, and heated at 5 °C/min from 25 to 1000 °C in 5%  $\text{H}_2$  in Ar gas mixture.

Laser Raman Spectroscopy (LRS) was performed at room temperature using the 647.1 nm excitation line of a Spectra Physics krypton ion laser. The beam was focused onto the samples using the macroscopic configuration of the apparatus. To avoid damage due to laser heating, all compounds were studied at a very low laser power (3 mW on the sample). To have a better signal/noise, four accumulations of each spectral range, have been done. No damage of the material by the laser was observed. The scattered light was analyzed with an XY Raman Dilor spectrometer equipped with an optical multichannel charge coupled device liquid nitrogen-cooled detector. The spectral resolution was  $0.5 \text{ cm}^{-1}$  in the  $130\text{--}1500 \text{ cm}^{-1}$  wavenumber range. Acquisition and data processing were performed with the LABSPEC software.

The specific surface area ( $S_{\text{BET}}$ ) of the catalysts was determined by nitrogen adsorption at  $-196^\circ\text{C}$  with Micromeritics ASAP2010 apparatus.

Scanning electron microscopy (SEM) and X-ray energy dispersive microanalysis (EDS) were carried out on HITACHI 4100S apparatus at 15 kV. Catalysts were ground as fine particles and mechanically dispersed on an electrically conductive carbon tape which was placed on an aluminum disc.

X-ray photoelectron spectroscopy (XPS) was carried out on Escalab 220 XL spectrometer (Vacuum Generators). A monochromatic Al  $K_\alpha$  X-ray source was used and electron energies were measured in the constant analyzer energy mode. The

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