

Performance evaluation of NiCo₂O₄ spinel as a catalyst for partial oxidation of methane

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ABSTRACT

The NiCo₂O₄ catalyst with spinel structure was prepared by a modified polymeric-precursor method using gelatin as an organic-directing agent. The obtained powder was characterized by XRD, TPR and tested on the partial oxidation of methane. The Rietveld analysis performed on the XRD pattern confirmed the crystallization of two phases, the spinel NiCo₂O₄, and a solid solution Ni_xCo_{1-x}O. TPR profile revealed that both phases are entirely reduced up to 610 °C. The catalyst showed CH₄ conversion of 75 % with H₂/CO ratio around 2 and no signal of deactivation by coke formation, such as confirmed by XRD and TG analysis carried out after the catalytic test.

Keywords: NiCo₂O₄, gelatin, partial oxidation of methane.

1. INTRODUCTION

Partial oxidation of methane has received much attention in recent years due to its advantages compared with other process used to syngas production, such as slight exothermicity, high conversion and selectivity, very short residence time and an H₂/CO molar ratio suitable for the methanol and Fischer-Tropsch synthesis [1-7]. Several catalysts have been studied in the reaction of partial oxidation of methane, among them the catalysts based on nickel [8], cobalt [9] and noble metals such as Pd [10], Pt [11], Ce [12], Rh, Ir and Ru [13]. Noble metals are significantly more expensive than transition metals, and its use as a catalyst become limited. Thus, catalysts consisting of transition metals have been widely investigated due to the relatively low cost and good activity [14,15].

Among the transition metals, nickel-based catalysts are far the most investigated materials for the partial oxidation of methane. Nevertheless, the deactivation by coke formation is still a problem to be solved, and several studies have been developed to improve the activity and the resistance to deactivation of nickel-based catalysts. The problem with deactivation may be addressed in different ways, and the two most promising strategies are the addition of alkali metals and the use of well-defined structures as catalyst precursors. The first strategy aims to increase the basicity of the catalyst and the second the dispersion of the active species, in both cases the result is a decrease of the coke formation [16].

OUAGUENOUNI *et al.* [2] observed a high catalytic activity to the reaction of partial oxidation of methane on NiMn₂O₄ spinel oxides that was related to the stability of the structure which led to the good dispersion of nickel species.

REQUIES *et al.* [3] reported that the addition of calcium and magnesium on Ni/Al₂O₃ catalysts im-

prove their performance to the reaction of partial oxidation of methane and reduce the deposition of carbon.

The authors observed that the addition of the alkaline earth metals increased the dispersion of nickel favoring a lower deposition of carbon.

In this paper, the activity, selectivity, and stability of NiCo₂O₄ catalyst were evaluated in the reaction of partial oxidation of methane.

2. MATERIALS AND METHODS

2.1 Synthesis

NiCo₂O₄ was synthesized by the modified Pechini method. The starting materials, nickel nitrate [Ni(NO₃)₂·6H₂O / Vetec], cobalt nitrate [Co(NO₃)₂·6H₂O / Vetec] and commercial gelatin Nutragel were used as purchased without any further purification. In a typical synthesis, 9 g of gelatin and 14.5 g of cobalt nitrate were dissolved together in distilled water and kept under constant stirring for 20 min at 40 °C. Then, 7 g of the nickel nitrate were added, keeping the solution under constant stirring at 80 °C until to form a polymer gel, that was subsequently heated at 350 °C for 4 h at a heating rate of 5 °C/min to produce a black powder. The black powder was ground in an agate mortar and finally calcined at 750 °C for 4 h in air atmosphere to crystallize the desired phase.

2.2 Characterization

The crystalline phases of the obtained sample, before and after the partial oxidation of methane, were determined by X-ray diffraction using a Shimadzu XRD 6000 diffractometer (CuK α radiation, 40 kV and 30 mA, 2 θ range 10°- 80° with step of 0.02° and a counting time per step of 2 °/min). The Rietveld refinement of XRD pattern was performed using the MAUD program version 2.26 to obtain the lattice parameters, the average crystallite size and the content of each identified phase. Temperature programmed reduction experiment was performed using a Micromeritics Autochem II 2920 on 25 mg of sample placed in a U-shaped quartz reactor. The catalyst was pre-treated by passing N₂ gas. A mixture of 10 % H₂/N₂ was then passed over the catalyst while the temperature increases to 1000 °C at a rate of 10 °C/min. A thermal conductivity detector analyzed the effluent gas after water trapping and permitted to quantify the hydrogen consumption. TG analysis was carried out in a Shimadzu TGA 50 analyzer under air atmosphere. The temperature range was between 25 °C and 900 °C using a heating rate of 10 °C/min and flow rate of 50 mL/min.

2.3 Catalytic tests

The catalytic activity test was performed in a fixed bed reactor using 100 mg of the catalyst which was diluted at a ratio of 10:1 (quartz: catalyst) at atmospheric pressure. The activation and reaction temperatures were 900 °C and 800 °C, respectively. Initially, a pre-treatment with a flow of N₂ carrier of 200 mL/min was carried out. Then, a mixture CH₄/O₂ was added where feed flow rates were 33.4 mL/min of CH₄ and 16.6 mL/min of O₂.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

The XRD analysis of the produced powder confirmed the formation of two distinct phases both showing well defined and intense diffraction peaks, what suggests a sample with high crystallinity. The diffraction peaks can be easily indexed to the cubic spinel structure NiCo₂O₄ (ICSD card number 24211) and the NiO with cubic structure (ICSD card number 9866). Fig. 1 shows the respective diffractogram including the graphical results of the Rietveld refinement. A good agreement between the experimental and calculated patterns was obtained, as can be seen in the Rietveld plot and confirmed by the good values of Rwp = 15 % and Sig = 1.167. The sample present 67,8 and 32.2 wt% of the phases NiCo₂O₄ and Ni_xCo_{1-x}O, respectively. The lattice parameters were 8.094 Å (NiCo₂O₄) and 4.196 Å (Ni_xCo_{1-x}O), while the average crystallite sizes found were 118.3 nm (NiCo₂O₄) and 142 nm (Ni_xCo_{1-x}O). However, despite the good quality of the refinement, it is worth noting the discrepancies observed between the diffraction peaks positions and the respective Bragg reflections obtained from the reference CIF files (see the top-right chart in Fig. 1). This may suggest variation in the composition of both phases and the crystallization of a Ni_xCo_{1-x}O solid solution instead of NiO. Indeed, it is widespread to determine the existence of a solid solution by the variation of the lattice parameters of the

NiO phase [17-21]. The molar composition of the solid solution ($\text{Ni}_{0.79}\text{Co}_{0.21}\text{O}$) was calculated using the Vegard's Law (Equation 1) [17].

$$\alpha_{SS} = \alpha_{CoO}(1 - x) + \alpha_{NiO}x \quad (1)$$

Where α_{CoO} e α_{NiO} are the lattice parameters of the phases CoO and NiO , respectively, α_{SS} is the lattice parameter of the solid solution, and x is the mole fraction of the phase NiO . The values of α_{CoO} e α_{NiO} were obtained from the respective crystallographic files, ICSD card number 9865 and ICSD card number 9866.

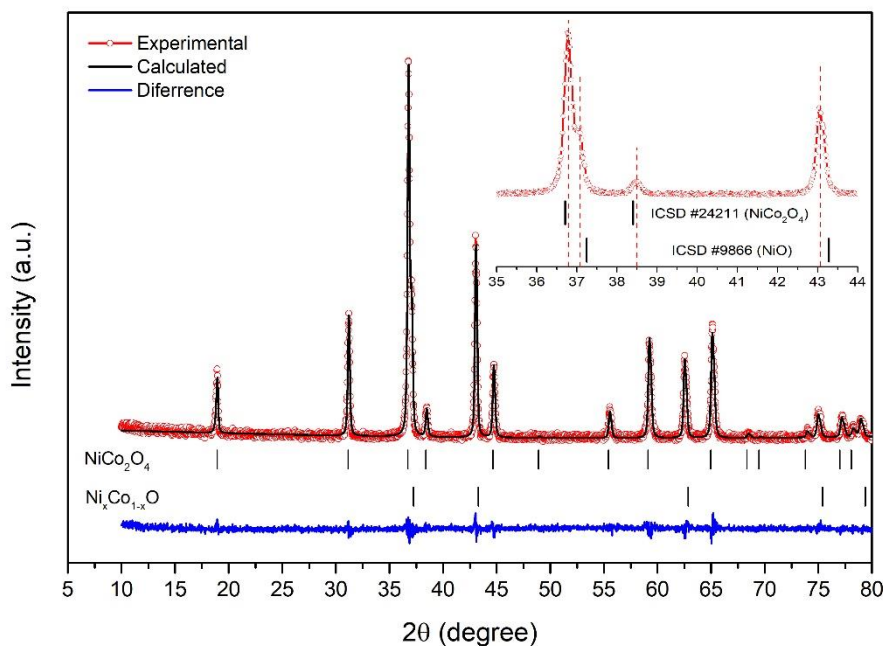


Figure 1: Rietveld refinement plot of the prepared sample showing the experimental, calculated and difference pattern. The Bragg reflections of the refined phases and ICSD cards are indicated by vertical bars in the main figure and the top-right chart, respectively.

3.2 Temperature Programmed Reduction

The H_2 -TPR profile of the produced sample is illustrated in Fig. 1. At least two H_2 consumption events are readily distinguished. It is worth noting that the H_2 consumption related to the first event, at low temperature, is substantially higher than that observed during the second event. This can suggest that the first event is related to the reduction of the spinel phase while the second event to the reduction of the solid solution $\text{Ni}_{0.79}\text{Co}_{0.21}\text{O}$. This is expected because the theoretical H_2 consumption of the spinel phase is four times higher than that calculated to the solid solution. Furthermore, the spinel phase content in the sample is about 67,8 wt%.

The low-temperature event observed in the range of 300 - 430 °C is associated to the reduction of Ni^{+2} to Ni^0 , Co^{+3} to Co^{+2} and Co^{+2} to Co^0 species in the spinel phase. This is consistent with results reported by TRIVEDI and PRASAD [22] and CAI *et al.* [23]. TAKANABE *et al.* [24] reported the presence of two overlapped peaks attributed to the simultaneous reduction of the phases Co_3O_4 and NiO in the CoNi (50:50)/ TiO_2 bimetallic catalyst. The authors also observed that all oxides of nickel and cobalt have been completely reduced up to 850 °C.

The high-temperature event observed in the range of 380 - 550 °C can be attributed to the reduction of the solid solution $\text{Ni}_{0.79}\text{Co}_{0.21}\text{O}$. This is consistent with the results reported by GOU *et al.* [25] that investigated the reducibility of Ni-Co-O bimetallic oxides. The authors observed a broadband in the region of 350 – 500 °C attributed to the overlapping of peaks related to the reduction of Ni^{+2} to Ni^0 and Co^{+2} to Co^0 .

Although unlikely, the interaction of the nickel and cobalt species with the quartz wool cannot be entirely ruled out. As a consequence, this could shift the temperature or even the profile of the reduction events, what makes a difficult task to determine precisely of the reduction mechanisms involved.

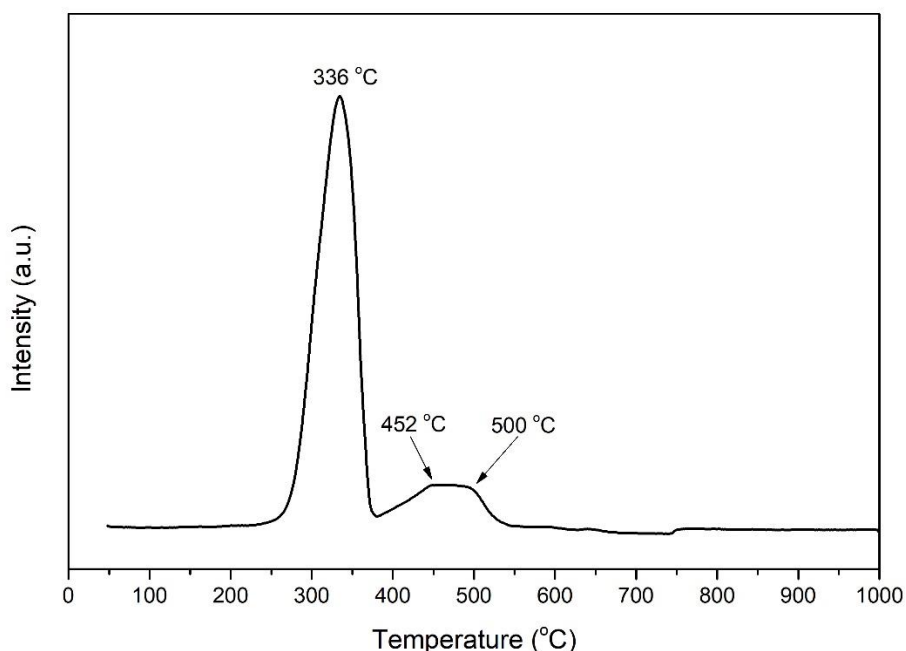


Figure 2: H₂-TPR profile of the produced sample.

3.3 Catalytic Test

The catalytic activity of the catalyst is shown in Fig. 3. The catalyst exhibited good stability during all reaction time presenting the methane conversion around 75%. It is well known that the reduction of nickel-based oxides may promote a better dispersion and particle size control of metallic nickel. Therefore, it is expected that the levels of methane conversion during the catalytic reforming are associated with the reduced nickel content. MATSUO *et al.* [26] studied CH₄/CO₂ reforming over a NiO-MgO solid solution and considered that the enhancement of methane conversion could be related to catalyst reducibility. PHONGAKSORN *et al.* [27] studied the performance of Ni-Co-based catalysts on the dry reforming of methane, and they found that the formation of a Ni-Co alloy may improve the resistance against coke formation. Some studies also report that the cobalt content can favor an increase of catalytic activity. CHANG-LIN *et al.* [28] prepared Co/Ce_{0.5}Zr_{0.5}O₂ catalysts varying the mass percent of Co and evaluated the catalytic performance to partial oxidation of methane. The authors showed that the activity of catalyst containing higher cobalt content is enhanced, possibly due to the formation more active centers. Moreover, the results indicated a higher resistance to deactivation by coke deposition.

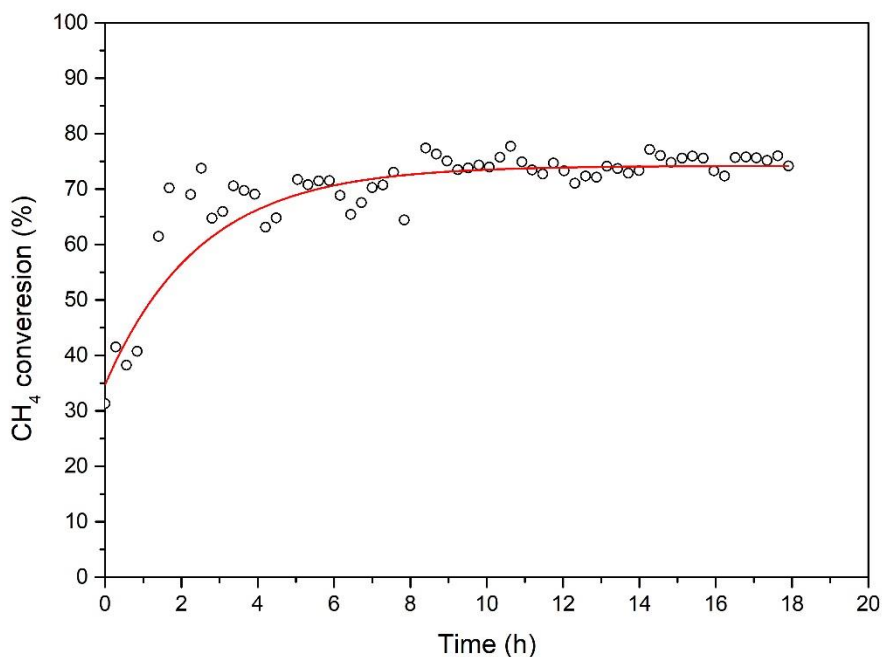


Figure 3: CH₄ conversion versus time on stream.

In Fig. 4a are displayed the selectivity towards CO and CO₂. The selectivity toward Co is high, about 85 %, what may be attributed the simultaneous occurrence of the reverse Water-Gas Shift Reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) and the reverse Boudouard reaction ($\text{C} + \text{CO}_2 \leftrightarrow \text{CO}$), both thermodynamically favorable at high temperatures. The H₂/CO ratio was around 2 (Fig. 4b) that is suitable for methanol and Fischer-Tropsch synthesis.

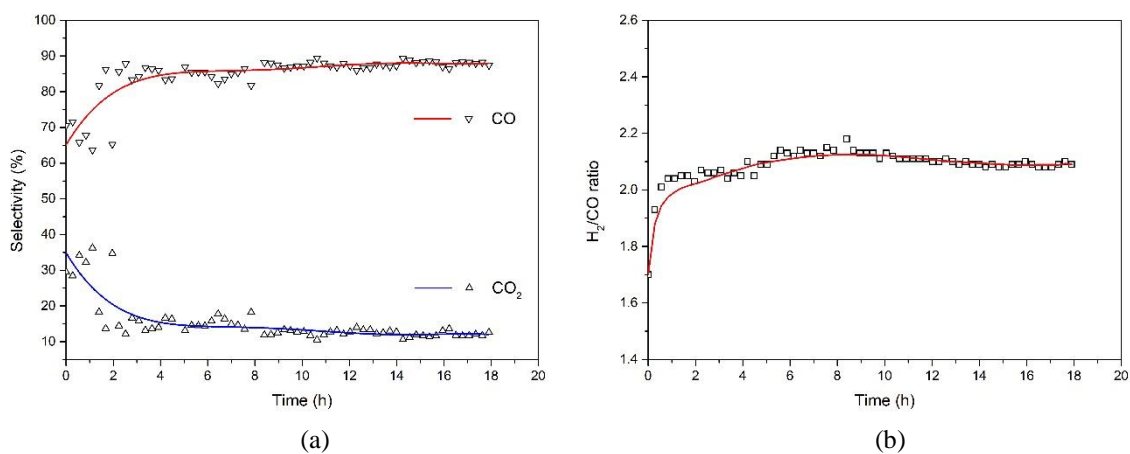


Figure 4: (a) CO and CO₂ selectivity and (b) H₂/CO ratio versus time on stream.

The sample tested in the partial oxidation of methane was characterized by XRD and TG analysis to identify the possible formation of coke. It can be seen in Fig. 5 (a) that the XRD pattern revealed the presence of a Ni-Co alloy and SiO₂ what agrees with the H₂-TPR results. The presence of SiO₂ is attributed to the quartz wool used as the catalyst bed. The TG curve (Fig. 5b) showed a mass gain around 2% associated with the oxidation of the nickel and cobalt metallic species.

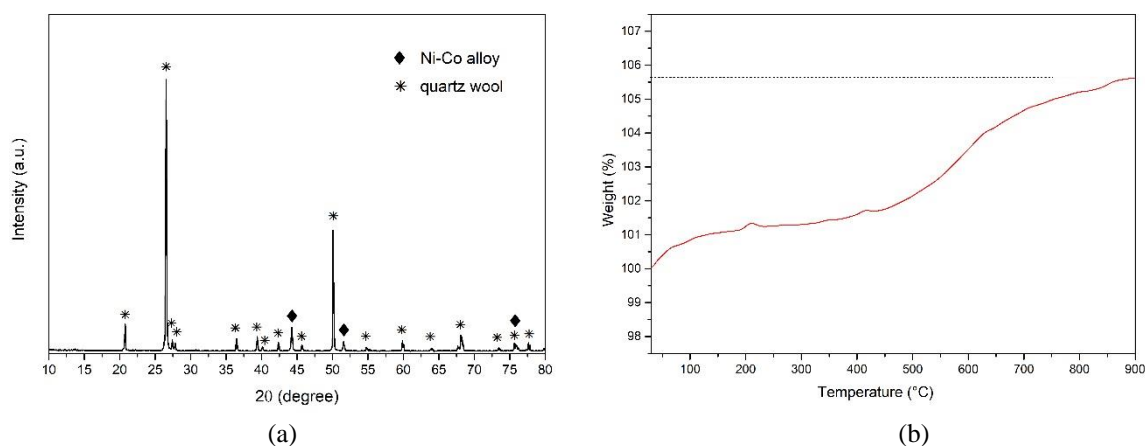


Figure 5: (a) XRD pattern and (b) TGA of the NiCo_2O_4 catalyst after reaction of partial oxidation of methane.

4. CONCLUSIONS

The catalyst prepared by using gelatin as an organic-directing agent presented two Ni-Co-based crystalline phases, a spinel-type structure, and a solid solution. XRD data confirmed the formation of both phases and the high crystallinity of the sample. The H_2 -TPR analysis showed that the complete reduction of the Ni-Co-based oxides occurs up to 610 °C. The catalytic tests revealed that the sample presents a good activity with high methane conversion and selectivity to CO. The XRD and TGA analyses carried out after the catalytic tests indicated that there was no coke formation. Finally, the results demonstrated that the good activity and coking resistance are probably related to the high crystallinity of the sample as well as the formation of a Ni-Co alloy.

5. ACKNOWLEDGEMENTS

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