Promoter Effect upon Activated Carbon-Supported Ni-Based Catalysts in Dry Methane Reforming

Juan Matos[*] and Maibelin Rosales

Engineering of Materials and Nanotechnology Centre, Venezuelan Institute for Scientific Research (IVIC), 20632, Caracas 1020-A, Venezuela.

Abstract

The influence of selected promoters such as Ca, Mg, Cu and Zn upon activated carbon-supported Ni-based catalysts in the dry methane reforming under mild experimental conditions (650ºC, 1 atm) was verified. It was found that Ni-Mg catalyst showed the highest initial catalytic activity followed by Ni-Ca/AC catalyst. As expected, catalysts promoted with the most basic oxides such as MgO or CaO showed moderate deactivation after 4h reaction ascribed to the basic Lewis behaviour which stabilize Ni-based catalysts.

Introduction

During the last decade, dry methane reforming (Eq. 1) has received much attention [1, 2] because this reaction is able to produce high purity synthesis gas (syngas) from natural gas.

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \qquad (1)$$
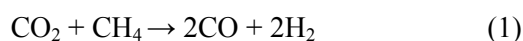
One advantage of dry methane reforming (DMR) is reducing a well-know greenhouse gas such as CO_2. An important decrease in the emission of CO_2 would be clearly beneficial to the environment [3, 4]. Syngas with different H_2/CO ratio have been employed in several industrial processes such as methanol, dimethyl ether or free-sulfur diesel and paraffines by Fischer–Tropsch synthesis [2, 5]. An Alternative low cost catalyst for methane reforming reactions is nickel-based catalysts [6]. In addition, activated carbon (AC) has showed appropriate characteristics as catalytic support [7, 8]. However, AC has been rarely employed as catalytic support for dry methane reforming [9-11] because it can suffer gasification by steam or by CO_2, through the reverse Boudouard reaction because both processes occur spontaneously at temperatures about 700°C.

The objective of this work is to study the influence of different promoters such as CaO, MgO, CuO and ZnO on the catalytic activity and stability of Ni-based catalysts supported on AC during DMR under mild experimental conditions.

Experimental

The catalysts were synthesized by successive incipient wetness impregnation of a commercial AC (Merck) with Ni, Ca, Mg, Cu and Zn nitrate solutions with the following compositions: NiO (5%), CaO (1 and 5%), MgO (1 and 5%), CuO (5%) and ZnO (5%). Solutions were heating on a stirring plate at 80°C until apparent dryness and drying at 120°C in static air oven for 3 h. The order of impregnation is given by the sequence of elements, i.e., Ni followed by Ca in Ni-Ca/AC [9]. Catalysts were characterized by XRD, XPS and adsorption-desorption N_2 isotherms at 77 K before and after 4 h reaction. Methane conversion was followed at mild experimental conditions (650°C, 1 atm) in a continuous flow system with a bed-fix quartz reactor [9-11]. 0.15 g of catalyst was loaded in the middle of the reactor and samples were submitted to an *in situ* pre-treatment before activity test under helium flow (50 mL·min^{-1}, 1 atm pressure) from room temperature up to 650°C with a heating rate of 10°C·min^{-1} and then remaining

*corresponding author. Email: jmatoslale@gmail.com

60min at 650°C [9]. CH_4 and CO_2 were introduced into the reactor (80mL.min^{-1} flow for both methane and carbon dioxide), and reaction was followed at 650°C. Analysis of methane was carried out with an on-line gas chromatograph with FID detection.

Results and Discussion

Fig. 1 shows the catalytic activity of Ni-based catalysts as a function of the reaction time. It can be seen with the exception of Ni(5%)-Cu(5%)/AC that most of promoted catalysts showed higher activity and better stability after 4h reaction than non-promoted Ni catalyst. It can be suggested that the better stability in promoted catalysts can be attributed to a lower interaction between NiO and AC consequence of the addition of suitable amount of promoters, mainly those with a clear Lewis base behavior such as MgO, CaO and ZnO. In previous works we have reported that the presence of CaO as promoter increased the dispersion of Ni nanoparticles [9-11]. This same behavior has been also recently found by Zhu and co-workers [12]. These authors found that the addition of promoters improved the catalytic performance, especially with the addition of CaO and MgO [12]. It can be noticed that the catalyst promoted with Mg showed the highest initial activity followed by that promoted with Ca. However, a different trend after 4 h reaction was found in the catalyst promoted with Ca, which showed higher activity after 4 h reaction in comparison with Mg-promoted catalysts. In addition, it can be seen that Zn-promoted catalyst did not suffer an important deactivation, only 18% after 4h reaction. Finally, it can be seen from Fig. 1 that Cu-promoted catalyst showed the lowest initial activity and about 50% deactivation after 4 h reaction which can be associated with a low basic behaviour of CuO. In short, Lewis bases as MgO, CaO and ZnO stabilize Ni-based catalysts during DMR [7, 9, 10]. Fig. 2 shows XRD patterns of catalysts after 4 h reaction. Besides of the diffraction peaks attributed to elemental Ni crystallites, it is important to point out the presence of two diffraction peaks at 52.0° and 77.0° attributed to Ni_3C formed by the interaction between carbon atoms and NiO [5, 9-11]. We suggest that both reduced Ni phases are responsible of the catalytic activity [11]. In addition, it must be remarked that the XRD patterns suggest that ZnO and CuO crystallites are reduced into Zn and Cu elemental phases which could be also became as active phases besides Ni and Ni_3C. By contrast, the most basic promoters such as MgO and CaO were able to form $MgCO_3$ and $CaCO_3$, which could be also responsible for the low deactivation after 4 h reaction by suppressing carbon deposits on the catalyst surface [9, 13]. Finally, a comparison of the BET surface area (S_{BET}) and micropore area of the catalysts is given in Table 1. For all catalysts, the BET surface areas were higher after 4 h reaction than in fresh catalysts. This increase has been previously reported by us for the case of Ca-promoted catalyst [11, 14] and it is attributed to the presence of the formation of a new molecular sieve of carbon with an important contribution of microporous. Also, as a consequence of the increase in surface area the diffusion of Ni nanoparticles from the carbonaceous matrix of the support to the surface is strongly induced with concomitant higher dispersion of Ni nanoparticles [11, 14]. Also, it can be seen from Table 1 that the addition of Lewis base promoters produce a clear increase in the micropore area and this increase is monotonic as a function of the weight of Mg or Ca promoters. This increase in surface area perfectly explain the low deactivation of catalysts [11, 14].

Table 1
Comparisons of textural properties of the catalysts

Catalyst	BET Surface Area ($m^2 \cdot g^{-1}$)		t-plot Microporous Area ($m^2 \cdot g^{-1}$)	
	Before reaction	After 4 h reaction	Before reaction	After 4 h reaction
Ni/AC	775	1083	701	967
Ni-Mg(1%)/AC	578	959	517	841
Ni-Mg(5%)/AC	326	880	274	718
Ni-Ca(1%)/AC	689	889	622	748
Ni-Ca(5%)/AC	482	873	422	738
Ni-Zn(5%)/AC	592	990	528	770
Ni-Cu(5%)/AC	595	869	531	751

A remarkable effect of CaO and MgO on initial catalytic activity and stability of Ni-based/AC catalyst was observed. Activity was attributed to the formation of nickel carbide phases while stability is attributed to the presence of carbonate phases and to a remarkable increase in the surface area.
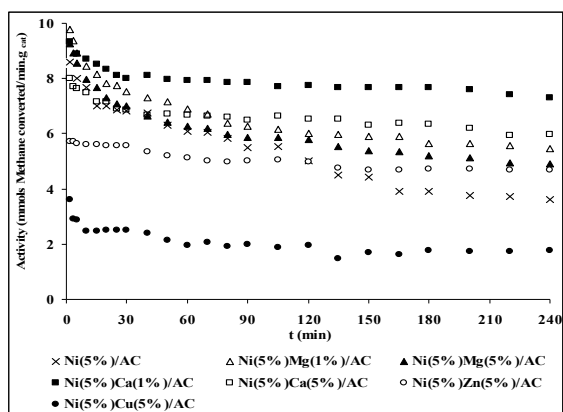

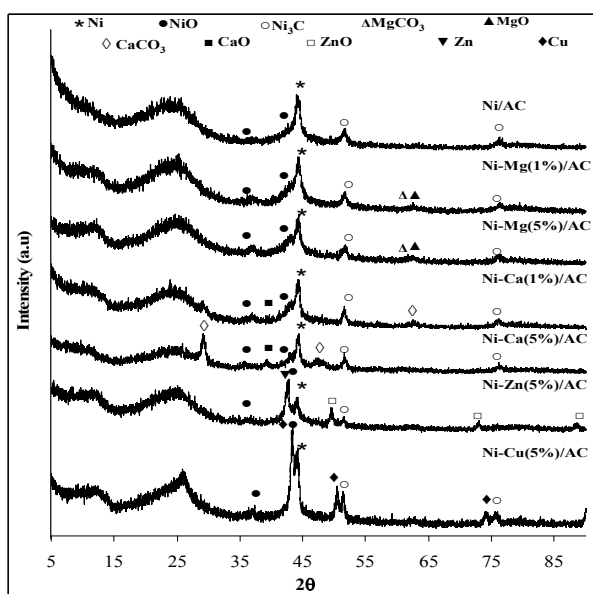Fig. 1. Catalytic activity of AC-supported Ni-based catalysts

Fig. 2. XRD patterns after 4 h of reaction of AC-supported Ni-based catalysts

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