Dry Methane Reforming on Carbon-Doped Nickel Foams
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Abstract
The catalytic activity of carbon-doped nickel foams in the dry methane reforming was studied at mild experimental conditions. The catalysts were synthesized by the controlled pyrolysis of different Ni-containing re-crystallized saccharose under N₂ flow. The results showed that carbon proportion clearly influences the catalytic activity of Ni-foams from low to moderate catalytic activity attributed to an in situ formation during pre-treatment of very active reduced Ni phases. It can be conclude that carbon-doped nickel foams catalysts prepared from the controlled pyrolysis of saccharose are interesting materials for natural gas conversion reactions.

Introduction
In the following years is expected an increasing production and conversion of methane because it is the main component of natural gas. Dry methane reforming (DMR) in Eq. 1, is an alternative route to obtain synthetic gas with less pollution for the environment [1-3] and with a low H₂/CO ratio (1:1), which is desirable for direct use as a feedstock for further syntheses of hydrocarbons or oxygenated hydrocarbons. On the other hand, DMR provides a route for disposing and recycling two important greenhouse gasses, CH₄ and CO₂ [4].

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad (\text{H}_2/\text{CO} = 1) \]  (1)

Noble metals catalysts are the most active in DMR [5] but due to the low availability and high price of such metals, an economical alternative are nickel-based catalysts [2-3, 6]. Supported Ni catalysts are a promising alternative to supported noble metal catalysts because of their high activity and low cost [7]. However, the most important limitation of Ni catalysts is the well-known deactivation by coke deposition along reaction. Carbon deposits produced according to methane cracking reaction in Eq.2 and CO disproportion reaction, Eq. 3, can cover the active centers and produce catalyst deactivation [8].

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]  (2)

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]  (3)

In addition, the science of carbon materials has receive an increase interest in the last years, and for the specific case of graphitic foams [9], this kind of carbon materials has received much attention because it has interesting thermal, magnetic and electronic properties. In this sense, the main objective of the present work was to study the influence of carbon doping upon the activity and stability of Ni-foams in the DMR under mild experimental conditions.

Experimental
Samples were synthesized by a modification of previous works [10-12]. In summary, catalysts were prepared by the controlled pyrolysis of saccharose by using a two-step procedure [10-12]. In a first step it was prepared an aqueous solution of 0.5 mL of nickel nitrate (Merck, analytical grade) with 5, 10, 20, 37, 50 wt.%. These solutions were added to 1.0 g of saccharose (Merck, bacteriology grade) and mechanical stirred at 80°C until the solution became viscous and light brown. Immediately, we remove the heat and left the solutions until the saccharide re-crystallizes as a homogeneous and

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Catalysts were denoted NW-Ni-w being w the weight (wt%) of nickel precursor in the solution. In a second step, a heat treatment was performed. It consists of a controlled carbonization [10] under an inert flow of nitrogen (200 mL·min\(^{-1}\), 20 psi) using the following step temperatures: 100, 150, 200 and 250°C with 30 min at each temperature, and finally 300, 400 and 450°C by 20 min at each temperature. Heating rate between steps was of about 8°C·min\(^{-1}\).

Methane conversion was followed at mild experimental conditions (650°C, 1 atm) in a continuous flow system with a bed-fix quartz reactor [2-3, 6]. 0.05 g of catalyst was loaded in the middle of the reactor. Samples were submitted to an in situ pre-treatment before activity test under Helium flow (50 mL·min\(^{-1}\), 14.5 psi pressure) starting at room temperature up to 650°C by 60 min, using a heating rate of about 10°C·min\(^{-1}\) [6]. CH\(_4\) and CO\(_2\) were co-fed into the reactor (80 mL·min\(^{-1}\)) flow of both methane and carbon dioxide, and reaction temperature was 650°C. Analysis of methane was carried out with an on-line gas chromatograph with FID detection. The fresh catalysts and after reaction were characterized by XRD and adsorption-desorption N\(_2\) isotherms at 77 K.

**Results and Discussion**

Fig. 1 shows the catalytic activity of nickel nanofoams as a function of the reaction time for the five catalysts tested. It can be seen that CH\(_4\) conversion clearly increase with the nickel content with a maxima of about 35 mmol·min\(^{-1}\)·g\(^{-1}\) of methane converted for the case of NW-Ni-37% followed by 33 mmol·min\(^{-1}\)·g\(^{-1}\) for NW-Ni-50%. These values are more than 3 times higher than that reported for bull Ni catalysts supported on a commercial activated carbon [1, 2]. By contrast, it can be seen that after 60 min, catalysts with less than 20% nickel were fully deactivated while NW-Ni-20% and NW-Ni-50% were deactivated after 3 h. Besides the highest activity, NW-Ni-37% showed the better stability, up to 4 h without deactivation. This low stability can be ascribed to the absence of Lewis bases as promoters [3, 4, 7] which are responsible to decrease the rate of the methane cracking reaction (Eq. 2).

The high initial activity of NW-Ni-37% and NW-Ni-50% can be attributed to an in situ formation of Ni reduced phases as can be inferred from the X-ray diffraction (XRD) patterns of nickel foams before and after 4 h reaction shown in Fig. 2 and 3, respectively. It can be seen from Fig. 2 that the main crystalline phase is NiO in all catalysts studied. The formation of this oxide is expected because the temperature of the thermal decomposition of nickel nitrate hexahydrate to nickel oxide is about 400°C [13]. By contrast, no diffraction peaks corresponding to NiO were observed in the XRD patterns of catalysts after reaction (Fig. 3). However, after reaction, XRD patterns showed three peaks at diffractions angles: 44.6°, 51.9°, and 76.4° which are attributed to elemental nickel (crystallographic card No. 04-0850, ICDD). In other words, we suggest that during reaction the reduction of NiO to Ni occurs by the interaction of NiO with carbon atoms from the doping and carbon atoms from the cracking of methane. This fact has been previously reported by us for the case of activated carbon-supported Ni-based catalysts [1, 2]. Ni may appear in the surface during the reaction to form the highly dispersed metal species increasing the active sites [14].

Finally, Table 1 shows a summary of the textural properties of selected Ni-foams obtained from the N\(_2\) adsorption-desorption isotherms. It can be observed that catalysts are mainly composed by mesopores as indicated the negligible micropore are in Table 1. However, it should be pointed out that in spite of the decrease of surface area (BET), after reaction there is a clear increase in the micropore area and a decrease in the mean pore width in NW-Ni-50%.
Ni-37%, the most active catalyst. This fact can be attributed with the formation in situ of a micropore carbon sieve probably by the activation with CO₂ of the carbon deposits from the methane cracking [1]. This fact is the focus of our present research.

Fig. 2. XRD of nickel nanofoams before reaction. (A) 20%wt. (B) 37%wt. (C) 50%wt.

Fig. 3. XRD of nickel nanofoams after reaction. (A) 20%wt. (B) 37% wt. (C) 50% wt.

Table 1

| Sample                      | \( S_{\text{BET}} \) (m\(^2\)/g) | \( \mu_{\text{pore}} \) (m\(^2\)/g) \(^b\) | \( W_p \) (nm) \(^c\) |
|-----------------------------|-----------------------------|----------------|----------------|
| NW-Ni-20%                   | 56.1                        | 0.96           | 28.4           |
| NW-Ni-37% before reaction   | 44.3                        | 1.76           | 36.9           |
| NW-Ni-37% after reaction    | (39.4)                      | (11.7)         | (29.1)         |
| NW-Ni-50%                   | 36.7                        | 4.12           | 39.7           |

\(^a\) Samples with less than 20% of Nickel in solution were not included because they presented negligible surface areas. \(^b\) Estimated from t-plot method. \(^c\) Estimated from Horvath Kawazoe method.

Conclusions

The highest initial activity and the best stability were found in the nickel foam prepared from 37%wt nickel nitrate solution. The high initial relative is attributed to the formation of elemental nickel and nickel carbides phases. The present results indicate that carbon-doped Ni foams prepared from the controlled pyrolysis of saccharose could be employed as interesting materials in catalysis.

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Received 15 August 2011