Short communication

The advantages of air addition on the methane steam reforming over Ni/γ-Al₂O₃

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Abstract

The effect of adding air to the feed in methane steam reforming over Ni/γ-Al₂O₃ was investigated. The catalyst exhibited a high specific surface area, but low metal surface area, with large Ni particles, which favor the deposition of carbon. A great quantity of carbon was seen to form on the catalyst during steam reforming, without any decrease in the reaction rate. This constant catalytic activity was consistent with the formation of filamentous *whiskers* of carbon during the process, verified by scanning electron microscopy. The addition of air decreased the energy consumed by the reaction and reduced significantly the carbon deposited on the catalyst during the process, making it a viable alternative for industrial application.
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1. Introduction

Today, hydrogen has emerged as a clean energy source offering an alternative to the fossil fuels. This gas can be directly burnt in an internal combustion engine or electrochemically converted to electricity in a fuel-cell system. Neither of these processes produces carbon dioxide, soot or carbon monoxide [1].

Electrolytic production of hydrogen with electricity generated by solar cells or hydropower has been regarded as the cleanest and most desirable method, but these processes do not supply enough hydrogen for current needs. Multi-step processing of hydrocarbon-based fuels is the most practical approach to the efficient production of hydrogen, and steam reforming of hydrocarbons has been widely employed in the chemical industry for this purpose. In particular, the reforming of methane with steam is the leading method of hydrogen production in the world [2–5], owing to the great volume of natural gas, consisting mainly of methane, produced annually.
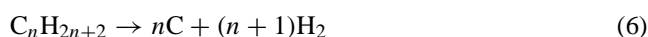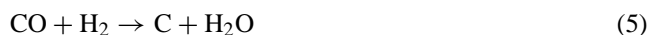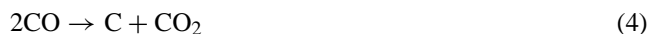
Steam reforming is outlined in Eqs. (1) and (2) [5]:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H = +250.1\,\text{kJ/mol} \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H = -2.8\,\text{kJ/mol} \quad (2)$$

This process is highly endothermic and is usually executed in a tubular reactor at 1173 K and 15–30 bar [6].

In industry, this is a catalytic process, in which the usual catalyst is nickel, supported on ceramic materials such as Al₂O₃, MgAlOₓ, Zr₂O₃, to which some stability promotor, is added, such as CaAl₂O₄, K₂O, or SiO₂ [5].

However, some potential problems can arise from the need to operate at high temperature. The thermal stability of the catalyst is certainly one, the steam tending to promote the sintering of the support and catalyst, but for a nickel catalyst, the main problem is coke formation, which follows the simplified mechanism below [3]:

$$CH_4 \rightarrow C + 2H_2 \quad (3)$$

$$2CO \rightarrow C + CO_2 \quad (4)$$

$$CO + H_2 \rightarrow C + H_2O \quad (5)$$

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2 \quad (6)$$

In fact, the need to minimize the deposition of coke is one of the biggest limiting factors for the industrial application of steam reforming. Considering reaction (5), the most obvious way to minimize coking is to increase the steam:carbon ratio, in order to favor the reverse reaction, and this method is used in industrial processes. However, the provision of steam at

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high temperatures is expensive, which tends to cancel out any significant economic advantage achieved by the reduced carbon deposition under stoichiometric conditions [3].

Apparently, this deposition during steam reforming of methane occurs predominantly by methane decomposition (reaction (3)). The catalytic production of hydrogen by methane decomposition was used in the past, consisting in the passage of methane alone over a metallic catalyst to form hydrogen and coke, the coke being deposited on the catalyst. After a predetermined time, the catalyst needs to be regenerated by passing air over it at high temperatures to burn off the deposited carbon, through reactions (7) and (8) [7]:

$$C + \tfrac{1}{2}O_2 \rightarrow CO \tag{7}$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \tag{8}$$

Making use of this concept, the aim in this investigation was to add air to the feed in the steam reforming of methane, with the reactor operating in conditions drastically favorable to coke formation ($H_2O:CH_4 = 0.25$), so as to remove the carbon formed, simultaneous to its deposition in the process.

2. Experimental

Nickel catalyst supported on γ-Al_2O_3 (13% by weight Ni) was made by wet impregnation of aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich Chem Co.) on γ-Al_2O_3 (Degussa.) previously calcined for 5 h in a stream of air at 823 K. After the impregnation, the catalyst was submitted to a further calcination in flowing air, for 10 h at 873 K.

The specific surface area (BET), total volume and average radius of pores were measured in a Quantachrome NOVA 1200.

The degree of reduction of the catalyst was evaluated by Temperature Programmed Reduction (TPR) (Micromeritics Pulse ChemSorb). The TPR was done with the temperature increasing at 10 K/min to 873 K, where it remained for 3 h, in 5% H_2/N_2 (AGA) flowing at 80 ml/min, simulating the real reduction conditions before a catalytic test. temperature programmed desorption of H_2 (TPD-H_2) was carried out in the same equipment, with H_2 adsorption occurring at 298 K, to measure the metal surface area.

Diffuse-reflectance infra-red spectroscopy (DRIFTS) of CO adsorption was performed on the reduced sample, to characterize the nickel metallic surface, using a Nicolet 750 IR spectrometer (Magna).

Steam-reforming experiments were done in a quartz fixed-bed microreactor (i.d.: 0.9 cm), at 873 K, fed with methane (AGA) flowing at 80 ml/min, 0.88 g/h of deionized water at 0.88 g/h, and air (20.3% O_2) at 0 ml/min, 16.26 ml/min, 32.52 ml/min, and 48.78 ml/min, corresponding to mole ratios of $H_2O/CH_4 = 0.25$ and $O_2/CH_4 = 0.00$, 0.04, 0.08, and 0.13, respectively. The experimental apparatus for the catalytic test is illustrated in Fig. 1. Before
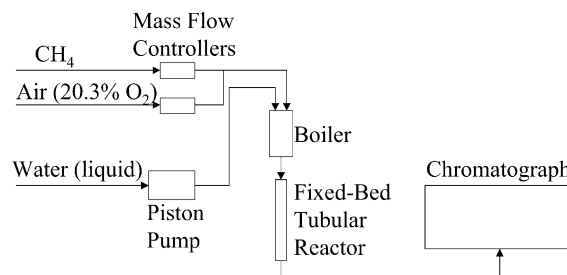

Fig. 1. Simplified scheme of apparatus used for the catalytic tests.

each test, the catalysts were reduced at 873 K for 3 h in situ in 5% H_2/N_2 flowing at 80 ml/min, at a temperature rising at 10 K/min. The tests were done continuously for 8 h, and the products analyzed by on-line gas chromatography (Varian GC3800). The chromatograph was equipped with two channels with one thermal conductivity detector each. One channel was composed of a serial Porapaq®-N and a 13X molecular-sieve packed column and used He as carrier gas, for the analysis of N_2, O_2, CH_4, CO, and CO_2. The other channel was composed of another 13X molecular-sieve packed column, using N_2 as carrier gas, for the analysis of H_2 and CH_4. The energy balance of the process was calculated to determine the change in enthalpy of the process (ΔH).

After each catalytic test, the used sample was submitted to thermogravimetric analysis (SDT 2960 Simultaneous DSC-TGA, TA Instruments), with synthetic air flow and a temperature ramp of 10 K/min up to 1273 K, in order to observe the burning of the carbon deposited on the catalyst during the catalytic test through reactions (7) and (8). Micrographs of the used samples were also taken, in a scanning electronic microscopy with secondary electrons (Zeiss DSM 940 A), to observe the morphology of the carbon deposited.

3. Results and discussions

Table 1 summarizes the basic measured properties of the catalyst.

As expected for a gamma-alumina supported catalyst calcined at low temperature, it can be seen that this catalyst has a high specific surface area. It also has the low degree of reduction and small metal surface area expected in an alumina-supported catalyst impregnated with a medium load of nickel and reduced at low temperature.

Table 1
Basic characterizations of catalyst

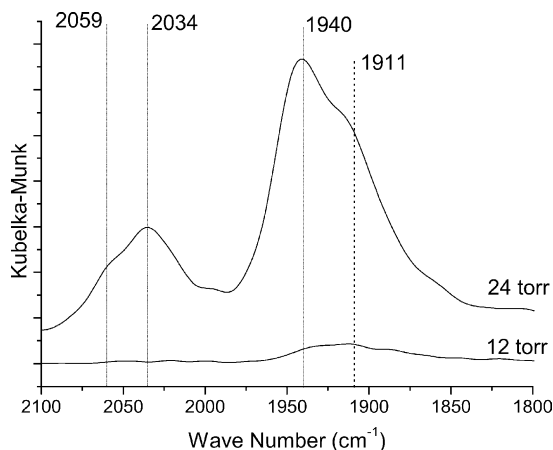|	
Specific surface area BET (m^2/g)	137
Total pore volume (cm^3/g)	0.32
Average pores radium (Å)	44.8
Degree of reduction (873 K for 3 h) (%)	29
Metal surface area (m^2/g)	2.0

Fig. 2. DRIFT spectra of CO adsorption on Ni/γ-Al$_2$O$_3$ at partial pressures of 12 and 24 torr.

Fig. 2 shows the results of DRIFT analysis of the catalyst. In the curve for CO adsorption at 24 torr, peaks can be seen, corresponding to adsorption metallic nickel, at 2059 cm^{-1}, 2034 cm^{-1}, 1940 cm^{-1}, and 1911 cm^{-1}. These relate to sub-carbonyl, linear carbon monoxide, bridged carbon monoxide on the (1 1 1) face and bridged carbon monoxide on (1 0 0), respectively [8]. These results show the predominance of CO bridge species, indicating larger particles, with average sizes much higher than 10 nm [8], which are also expected in an impregnated catalyst reduced at low temperature. It is well known that carbon deposition on the catalyst during steam reforming of methane is favored on large particles [3].

The conversion of methane observed in the steam-reforming experiments is plotted in Fig. 3 against time on stream, for each of the air/methane mixtures described above.

In this figure, the conversion is seen to increase with increasing O$_2$:CH$_4$ ratio. This is to be expected, as the process is limited by the quantity of water in the feed, which is less than stoichiometric, and the excess methane can decompose to form coke (reaction (3)). The O$_2$ introduced as air effectively oxidizes this excess methane, either partially (reaction (9)) or totally (reaction (10)), through the removal, by the oxygen, of the carbon adsorbed on the catalyst (reactions
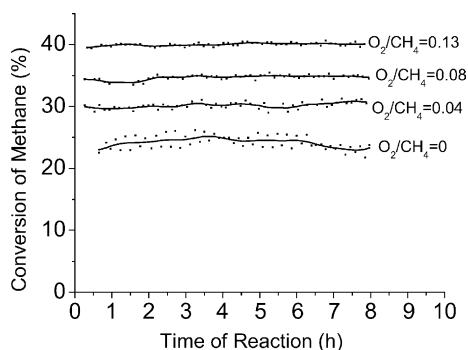

Fig. 4. H$_2$/CO mole ratio in product stream vs. O$_2$/CH$_4$ ratio on feed stream.

(7) and (8)) [5]:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2, \quad \Delta H_{298} = -35.7 \, \text{kJ/mol} \tag{9}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H_{298} = -890.3 \, \text{kJ/mol} \tag{10}$$

The occurrence of partial oxidation causes a decrease in the H$_2$/CO ratio in the products with rising O$_2$/CH$_4$ ratio, as illustrated in Fig. 4, given that the H$_2$/CO ratio of this reaction is lower than that of steam reforming.

However, because these oxidation reactions are exothermic, the addition of air brings the great benefit of a decrease in ΔH, as shown in Fig. 5. The combination of steam reforming and partial oxidation of methane is named autothermal reforming of methane, and is strongly recommended for the generation of hydrogen for use in fuel cells [2,5]. Thus, it is of considerable importance to study the stability of autothermal reforming against carbon deposition on base metal catalysts, and that is the main intention of this work.

After the catalytic tests, the samples were submitted to thermogravimetric (TGA) analysis to determine the amount of carbon formed. The total loss of mass relative to the mass of catalyst, attributed to the removal of accumulated carbon,

Fig. 3. Conversion of methane vs. reaction time for each O$_2$:CH$_4$ mole ratio used in the feed stream at 1 bar and H$_2$O/CH$_4$ = 0.25.
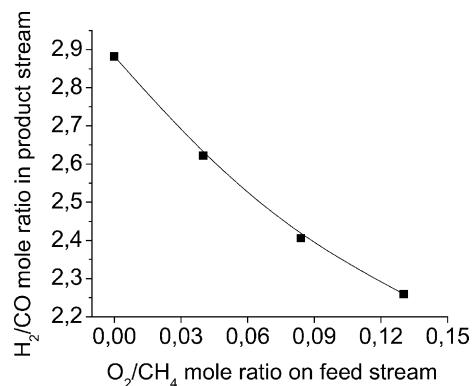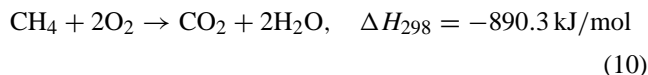

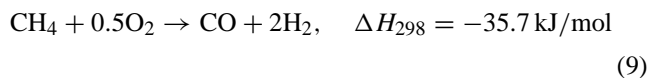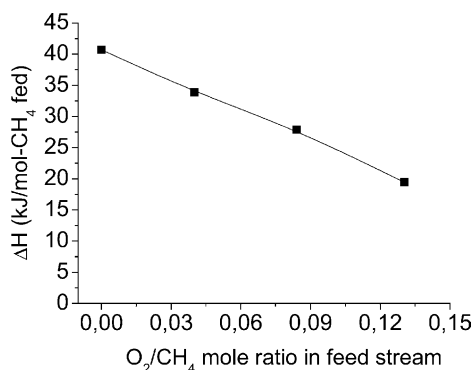Fig. 5. ΔH of process per mol of methane in reactor feed vs. O$_2$/CH$_4$ mole ratio in feed stream.
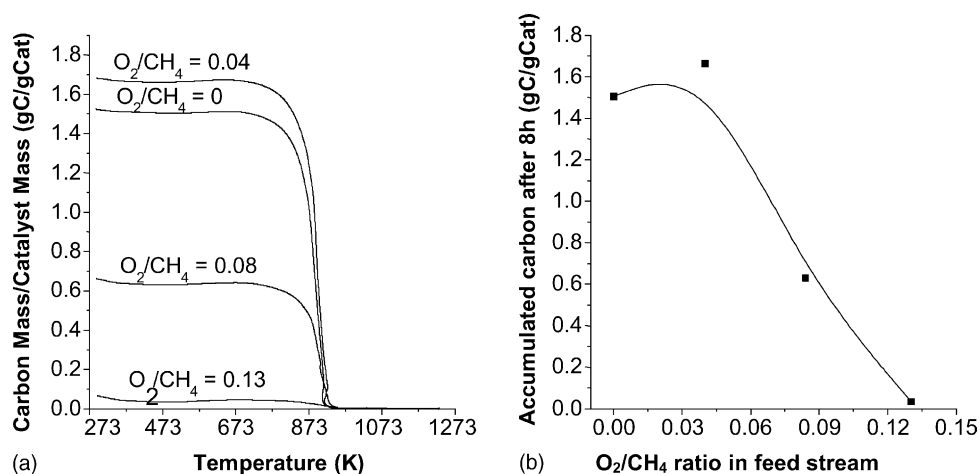
Fig. 6. Carbon accumulated on Ni/Al$_2$O$_3$ catalysts after 8 h of steam reforming, with air added, as a function of O$_2$/CH$_4$ mole ratio in feed stream: (a) TGA of the carbon deposit and (b) accumulated carbon, after reactions.

is shown in Fig. 6. The addition of air (and consequently O$_2$) to the feed decreased drastically the amount of carbon formed on the catalyst, approaching 0% at an O$_2$/CH$_4$ ratio of 0.13, which indicates that, at higher O$_2$:CH$_4$ ratios, with a H$_2$O/CH$_4$ ratio of 0.25, carbon deposition would not occur in autothermal reforming of methane. This also provides strong evidence that this process will reliably avoid coke formation at higher contents of H$_2$O and O$_2$ in the feed. Operation of the reactor at higher contents of these reactants is necessary in practice to raise the yield of H$_2$, although in the present study methane was used in excess to simulate drastic conditions of deactivation.

Thus, it can be concluded that the addition of air to the steam-reforming feed results in a decrease in the amount of carbon formed on the catalyst. On the other hand, even in the experiment with no air, in which a heavy deposit of carbon was observed, it can be seen in Fig. 3 that methane conversion did not decrease during 8 h of reaction. It is known that the formation of carbon involves a carbide cycle and consists of two to three steps: the first step is the formation of a monolayer of carbon atoms through an intermediate carbide-like compound. This species is highly reactive and easily removed. The second step includes the formation of a graphite phase by polymerization of the carbon atoms, when they are in excess. These graphite deposits can accumulate over the metal surface, deactivating it. In metal particles bigger than 5 nm, a third step can occur, in which the high concentration of carbon at the top surface causes a concentration gradient between this surface and the bottom of the particle, which leads to carbon diffusion across the nickel crystal. The carbon concentration at the front of the metal particle is close to that in Ni$_3$C, while that on the opposite (1 1 1) face of the particle (site bottom) is equal to that in a saturated solution of carbon in nickel. Thus, the diffusion goes from the top surface to the base of the nickel crystal, where it is bonded to the support, causing the growth of a carbon filament (*whisker*) on the support, ending at the

dislodged crystal. Although the growing filament leaves the nickel site active, it gradually fills the spaces in the bed and blocks the reactor, raising the internal pressure to unacceptable levels [3,6]. Thus, as the rate of conversion does not change during the catalytic test, it can be inferred that the carbon is deposited predominantly in the form of filaments during steam reforming. Fig. 7(a) shows micrographs of a sample submitted to steam reforming without the addition of air, which verify the hypothesis of carbon filament formation, as the deposit consists mainly of this phase.

The average diameter of carbon filaments shown in Fig. 7(a) is around 150 nm. According to the hypothesis that these filaments are formed by diffusion of carbon through the crystal to the metal–support interface, the particle diameter should be of the same order as that of the carbon filament formed under it. So it is probable that the metal particles of catalyst in question have diameters around 150 nm.

However, the Fig. 7 shows a decrease in the diameter of the filaments, with the increase of the O$_2$/CH$_4$ mole ratio, which is also presented in Table 2.

It is well known that the carbon does not deposit so easily in small particles, because the formation of filaments require a great amount of near nickel active sites, in order to initiate polymerization. With smaller particles, the possibility of polymerization decreases, becoming easier the gasification of the carbon than its polymerization [3].

The decrease in the diameter of the filaments of carbon with the increase in the O$_2$/CH$_4$ molar ratio indicates that there is a decrease in the average diameter of the active

Table 2
Average diameter of carbon filaments

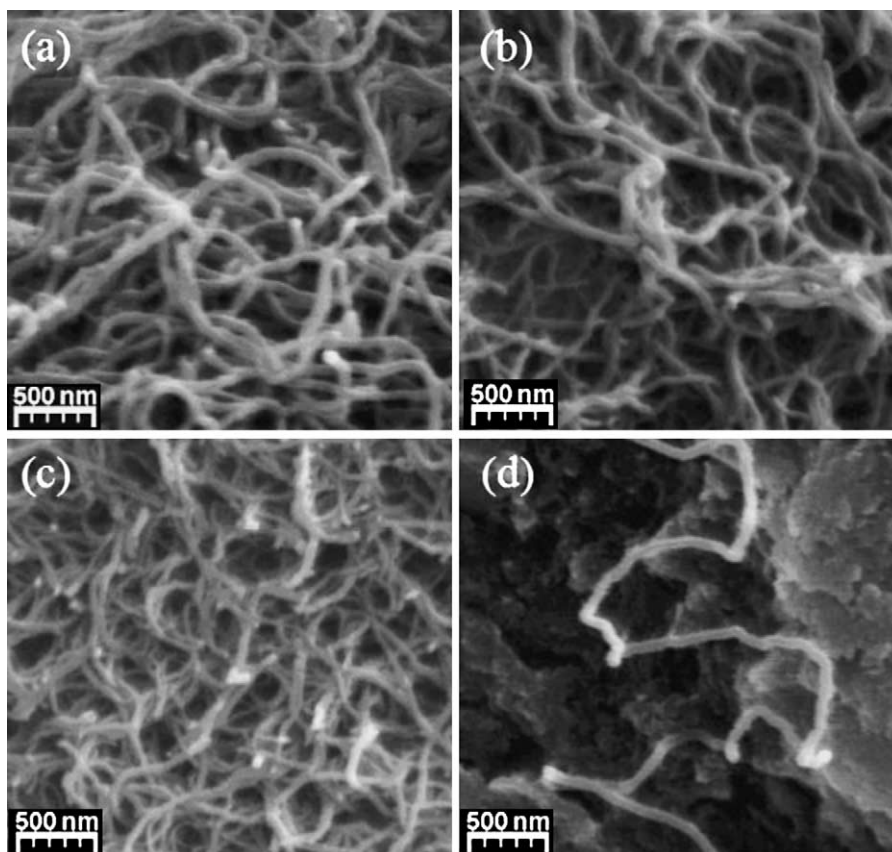| O$_2$/CH$_4$ mole ratio	Average diameter (nm)
0	150
0.04	100
0.08	70

Fig. 7. Scanning electron microscope image of Ni/Al_2O_3 after 8 h of steam reforming, with magnification of 30,000×. Ratio O_2/CH_4: (a) 0; (b) 0.04; (c) 0.08; and (d) 0.13.

particles of metal, due to the presence of oxygen (ensemble size control). This decrease occurs because of the bonding of oxygen with nickel, limiting the active region to methane adsorption, exactly how sulfur works during the SPARG process (Sulfur Passivated Reforming) [3]. Therefore, above a determined amount, oxygen inhibits the polymerization of carbon, which is a fundamental step for filament formation, thus inhibiting the coke deposition. This is observed on the Fig. 7(d) with the ratio $O_2/CH_0 = 0.13$ and from the thermogravimetric analysis, presented on Fig. 6.

4. Conclusion

The addition of air to the feed in the steam reforming of methane offers some advantages.

The first is a decrease in the amount of carbon deposited on the catalyst, attributable to the ensemble size control by oxygen, which covers a fraction of the nickel surface, decreasing the particle size, and inhibiting the polymerization of carbon and, consequently, its accumulation.

Another advantage of adding air to the feed is that the endothermicity of the process is reduced, so that hydrogen may be generated without consumption of external energy, making it viable to produce this gas for use as a fuel. Steam reforming combined with partial oxidation of methane is termed autothermal reforming of methane; a potential application is the production of hydrogen as a fuel and it has the great advantage of avoiding the deposition of carbon on the catalyst.

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