

Preparation and evaluation of Co/Al₂O₃ catalysts in the production of hydrogen from thermo-catalytic decomposition of methane: Influence of operating conditions on catalyst performance

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Abstract

This paper presents the synthesis of Co-doped Al₂O₃ catalysts, developed by our group, with porous structures and high surface areas. The catalytic activity of the materials obtained was evaluated in the catalytic decomposition of methane, which is an attractive method for CO/CO₂-free production of hydrogen, particularly for fuel cell applications.

The catalysts were shown to be active and stable in relation to the catalytic decomposition of methane reaction. It was observed that the catalytic performance is dependent on the catalyst characteristics and on the operational conditions employed.

The conversion of methane increased with metal loading, reaction temperature and N₂:CH₄ molar ratio.

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1. Introduction

With the forecast of an exhaustion of oil resources, which has been predicted to occur in a few decades, and the climate change associated with the emission of greenhouse gases, there is an urgent need for alternative energy sources, capable of assuring both the supplying of an increasing world-wide demand and the assurance of the proper protection of the environment. In this regard, hydrogen appears to be an efficient alternative energy source, mainly when used for fuel cell applications. The hydrogen fuel cell is capable of generating energy with a high efficiency and low noise levels and it releases to the atmosphere only water vapor instead of CO, CO₂, black smoke and other forms of pollutants [1–3].

There are a lot of opportunities for catalysis to participate in the economic production of hydrogen. One method of hydrogen production is through the direct catalytic decomposition of methane. Unlike other conventional hydrogen production methods, such as methane steam reforming and methane partial oxidation, which produce a mixture of hydrogen and carbon oxides, catalytic cracking has as the major advantage the possibility of obtaining a H₂-rich gas effluent, free from CO and CO₂, eliminating the necessity for the separation of hydrogen from the other gaseous products. This significantly simplifies the process and reduces overall CO₂ emissions and makes it particularly attractive for fuel cell applications. However, the catalytic decomposition process could also present some problems associated with the catalytic deactivation due to carbon deposits forming on the catalyst surface [4–9]. Therefore, the development of active and deactivation resistant catalysts becomes an interesting challenge.

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Several authors have reported studies on the methane decomposition reaction for hydrogen production promoted by metal supported catalysts. Most of these metal supported catalysts for methane decomposition reported until now were prepared by impregnation of commercial supports with a solution of the salt of the active component or by co-precipitation of salts of the active component and a textural promoter [1,7,9,10–17]. Hydrogen production through methane conversion at 650 °C over Ni-supported zeolite and Ni-supported silica catalysts has been investigated by Inaba et al. [11]. A maximum CH₄ conversion of 45% was reported and the Ni-supported USY-type zeolite was found to have a longer catalytic lifetime (remaining active for around 6 h) than the Ni-supported silica catalyst. The authors suggested that the smaller diameter of the nickel particles, the lower amount of solid acid and the larger outer surface area of the support lead to nickel-supported catalysts having a greater amount of carbon deposited on the surface with the catalytic activity eventually stopping completely. Bai et al. [18] have studied the methane decomposition reaction over activated carbon and alumina in the temperature range of 1023–1173 K and the volumetric hourly space velocity (VHSV) was from 3.0 to 18.0 L g⁻¹ h⁻¹. For all catalysts methane conversion shows the highest value of 25–35% at the beginning of the reaction and then gradually decreases during the reaction period (120 min). The pore size change during the course of the methane decomposition over activated carbon indicates that the catalytic reaction occurs mainly in the micropores. Activated alumina has different pore properties and carbon deposition in the alumina mesopores is responsible for the catalytic activity. The carbon deposition on activated carbon shows either carbon filaments or agglomerates according to the different sources of activated carbon.

However, novel routes have been proposed and explored in the preparation of several heterogeneous catalysts for application in a great variety of reactions. Properties such as pore size, pore size distribution, surface area and pore vol-

ume are important for the application of these catalysts because they are directly related to the performance, acting on the conversion of reactants and on the product selectivity [19–21]. In this context, this paper presents the synthesis of Co-doped Al₂O₃ catalysts with porous structures with a high surface area. Cobalt was used as the active phase due to its availability and accessible cost. The synthesis method for the catalysts, developed by our group, consists of obtaining an intermediate hybrid compound of aluminum, cobalt and the organic polymer chitosan. The influence of chitosan as an organic precursor in the material preparation has been investigated in the synthesis of a great variety of ceramic powders [22]. Chitosan, a (1–4)-linked 2-amino-2-deoxy-β-D-glucopyranose, is a polymer derived from chitin. The presence of amine and hydroxyl groups in the polymeric chitosan structure may help greatly in the metal cluster formation. In addition, the polymeric structure can inhibit the metal particle sinterization process during annealing treatment, which is a consequence of the great distances between metal clusters in the intermediate hybrid polymer [22,23]. Through the polymer elimination by thermal treatment, the Co/Al₂O₃ catalyst is obtained. With the aim of highlighting the enhancement of catalytic properties, the catalysts obtained were tested in the decomposition of methane reaction for hydrogen production and the results are reported here.

2. Experimental

2.1. Catalyst preparation

For the preparation of the Co/Al₂O₃ catalysts (Fig. 1), 3.0 g of chitosan (C₆H₁₁O₄N)_n (Aldrich) were dissolved in 100 mL of acetic acid solution (5% v/v) and 9.20 g of Al(NO₃)₃ · 9H₂O (Riedel-de-Haën) were dissolved in 40 mL of distilled water.

The Al aqueous solution was then added to the polymer solution with stirring. The chitosan monomer to Al molar ratio was 1.5:2. The Al-chitosan solution was added into a

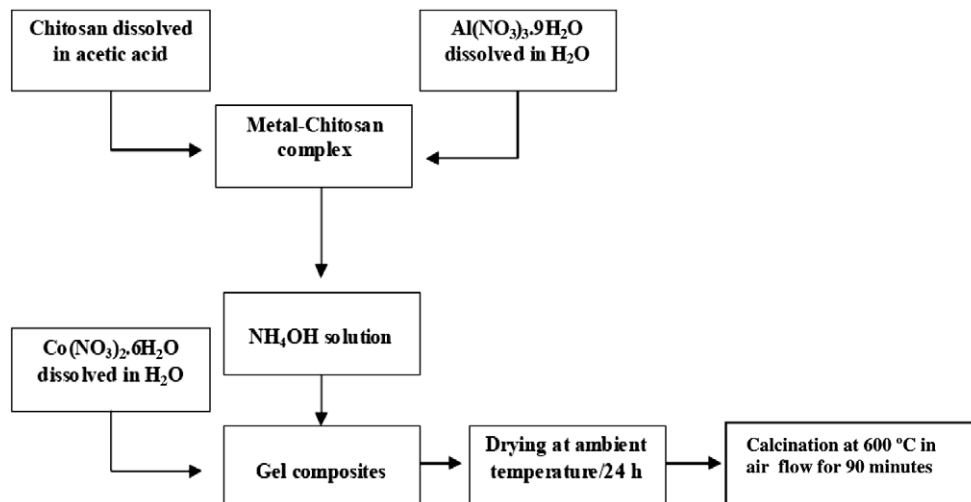


Fig. 1. Flowchart of the synthesis of the Co/Al₂O₃ catalysts.

NH_4OH solution (50% v/v) under vigorous stirring. The Co addition (4, 12 and 20 wt.%) was carried out by impregnation of the gel composites formed with an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel-de-Haën), in the appropriate concentrations, with stirring, for 6 hours. The samples impregnated with Co were removed from the solution and dried at ambient temperature for 24 h. The $\text{Co}/\text{Al}_2\text{O}_3$ samples were obtained by annealing the dried samples at 600 °C in air flow for 90 min with a heating rate of 5 °C min^{-1} .

2.2. Catalyst characterization

Samples were characterized (before and after the catalyst tests) by N_2 adsorption/desorption isotherms obtained at the temperature of liquid nitrogen in an automated physisorption instrument (Autosorb-1C, Quantachrome Instruments). Prior to the measurement, the samples were outgassed under vacuum at 200 °C for 2 h. Specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method and the pore size distributions were obtained according to the Barret–Joyner–Halenda (BJH) method, from the adsorption data.

For the determination of the Co content an atomic spectrometer (Varian Model SpectrAA 50), equipped with an air-acetylene flame atomizer and a Hitachi cobalt hollow cathode lamp (HLA-4S) was used.

The crystalline phases of freshly prepared catalysts were characterized by X-ray diffraction (XRD) in a Siemens D-5000, with graphite monochromated $\text{Cu K}\alpha$ irradiation.

The sample morphologies were observed (before and after the catalytic tests) on scanning electron micrographs, obtained with a Philips XL30 scanning electron microscope operating at an accelerating voltage of 20 kV.

2.3. Catalyst testing

The decomposition reaction of CH_4 was carried out in a quartz-tube fixed bed flow reactor (12 mm inner diameter) heated by an electric furnace (Fig. 2). The $\text{Co}/\text{Al}_2\text{O}_3$ catalysts (50 mg) were pre-treated in situ in a H_2 stream at 700 °C with a heating rate of 10 °C min^{-1} for 1 h. The experiments were conducted under atmospheric pressure at 600, 700 and 800 °C. The reaction gas was composed of N_2 and CH_4 in 2.5:1; 4:1; 6:1 and 1:9 molar ratios ($\text{N}_2:\text{CH}_4$). The total flow rate of the reaction gas was 35 mL min^{-1} , which corresponds to a space velocity of 42 mL $\text{h}^{-1} \text{g}^{-1}$ catalyst. The reactant and the product gases were analyzed with a Shimadzu GC-8A gas chromatograph, equipped with a thermal conductivity detector, a Porapak-Q column and a 5A molecular sieve column with Ar as the carrier gas. The N_2 in the reaction gas was used as a diluent and as an internal analysis standard. Catalytic activity was evaluated in terms of methane conversion. We defined methane conversion as

$$C_{(\text{CH}_4)} = (Q_{\text{conv}}/Q_{\text{CH}_4}) \times 100\%, \quad (1)$$

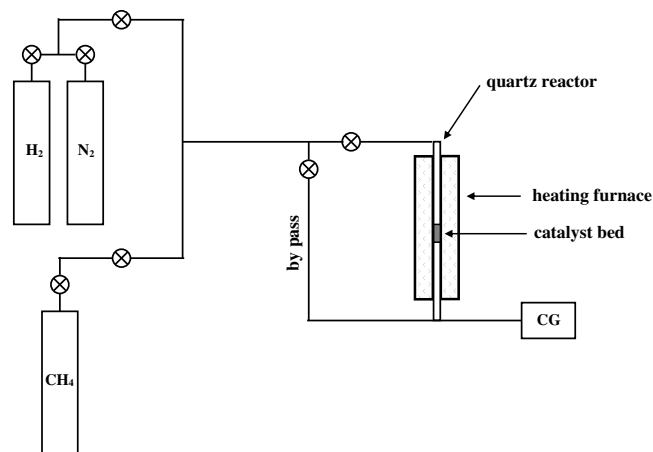


Fig. 2. Schematic diagram of the reactor system.

where Q_{conv} represents the quantity (moles) of converted methane; Q_{CH_4} represents the total quantity (moles) of methane fed into the reactor.

3. Results and discussion

3.1. Characterization of catalysts

The chemical analysis, BET specific surface area and pore size distribution values of all the $\text{Co}/\text{Al}_2\text{O}_3$ catalysts are summarized in Table 1. It can be observed that there was a significant difference between the theoretical and actual metal content, obtained experimentally, indicating that the synthesis method used did not result in an efficient impregnation of the metal in the support.

On comparing the values for the specific surface area (BET) of the catalysts impregnated with 2%, 6% and 9% of Co and Al_2O_3 without impregnation, prepared by the same method, it was found that the values for the catalysts with 2% and 6% of Co were close to those for pure Al_2O_3 and the greatest decrease occurred for the sample with 9% of Co. The same behavior was found for the pore volume decrease. Of all the catalysts prepared, 6-Co/ Al_2O_3 showed the highest BET surface area, 336 $\text{m}^2 \text{g}^{-1}$. In general, the BET surface area values decreased with an increase in metal loading. Thus, the catalyst with the highest metal loading (9-Co/ Al_2O_3) showed the lowest BET surface area of 252 $\text{m}^2 \text{g}^{-1}$. The pore volume also decreases with an increase metal loading. Such changes can be attributed to the impregnation step that causes a partial pore filling

Table 1
Chemical analysis and surface properties measured by N_2 physisorption

Catalysts	Co (wt.%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{BJH} ($\text{cm}^3 \text{g}^{-1}$)
Al_2O_3^a	–	343	0.651
(4%)-Co/ Al_2O_3	2	323	0.459
(12%)-Co/ Al_2O_3	6	336	0.494
(20%)-Co/ Al_2O_3	9	252	0.362

Co (wt.%) = cobalt loading, S_{BET} = specific surface area and V_{BJH} = pore volume.

^a T_c = calcination temperature (550 °C).

and consequently a decrease in BET surface area and pore volume values due to the cobalt addition. The results for the X-ray diffraction analysis of the catalysts are shown in Fig. 3. According to the literature, the diffraction peaks at $2\theta = 32^\circ, 37^\circ, 45^\circ, 60^\circ$ and 66° can be attributed both to the Co_3O_4 of the spinel structure and the CoAl_2O_4 (cobalt aluminate), since the diffraction patterns of the two oxides are very close. As expected, an increase in the cobalt content caused an increase in the intensity of the main diffraction peak at $2\theta = 37^\circ$, suggesting a better crystal formation. For the higher cobalt contents signals at $2\theta = 32^\circ, 37^\circ$ and 60° were observed, also relating to the cobalt oxide (Co_3O_4), making the identification of its structure more complete. It was also observed that the peaks of $\gamma\text{-Al}_2\text{O}_3$, notably at $2\theta = 46^\circ$ and 67° , became less intense with the increase in the cobalt content.

3.2. Catalyst testing

In order to investigate the catalytic activity of the Co/ Al_2O_3 catalysts the decomposition reaction of methane was carried out. The reactions were run for 240 min, except for the catalytic stability test which was carried out for 450 min. No methane decomposition products other than hydrogen were detected in the effluent gas during the experiments. Thus, carbon and hydrogen can be regarded as the only products of methane decomposition, that is, only the following global reaction occurs during the process:

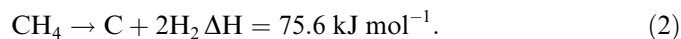


Fig. 4 shows the catalytic behavior of the materials with several metal concentrations as a function of the reaction temperature. When the tests were conducted at 600°C , none of

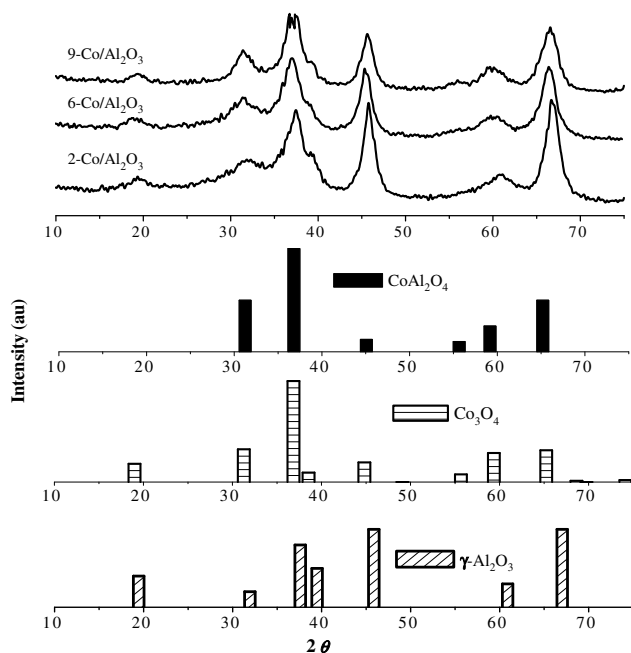


Fig. 3. X-ray diffraction patterns for the Co/ Al_2O_3 catalysts after the calcination step.

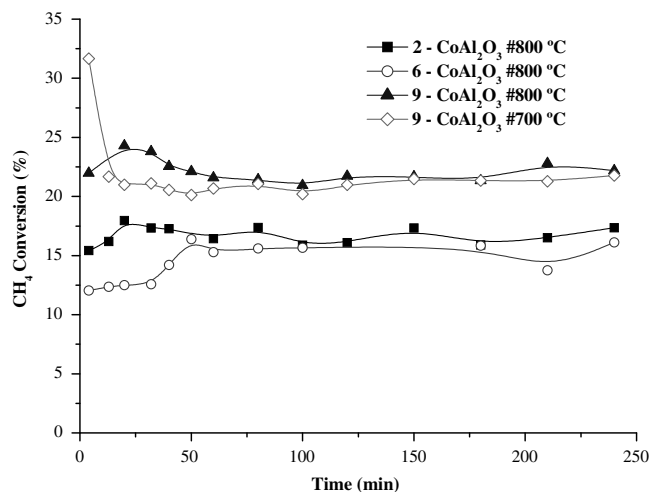


Fig. 4. Methane decomposition over Co/ Al_2O_3 catalysts. Performance of the catalysts in the CH_4 conversion with time-on-stream at different temperatures. $\text{N}_2:\text{CH}_4 = 6:1$.

the Co-based catalysts showed activity. However, when tests were preformed at 700°C , only the 9-Co/ Al_2O_3 catalyst showed activity, indicating the catalytic action of the active phases of the metal (present at higher concentration in this catalyst) even at this temperature. Only at the highest reaction temperature of 800°C did all catalysts show activity in the methane decomposition process. For all catalysts methane conversion showed values of approximately 15–22%. The highest methane conversion values were achieved by the catalysts with the highest amount of Co loading, suggesting that in the presence of Co, the catalyst becomes more active and the active metal site is responsible for the breaking of the carbon–hydrogen bonds in the CH_4 cleavage to produce H_2 . The highest activity of the 9-Co/ Al_2O_3 catalyst at the beginning of the reaction at 700°C is followed by a rapid drop and then a very smooth decrease until a steady state is reached which remained stable until the end of the run (240 min). This behavior may be related to the carbon deposition that promotes a blocking of the active surface [18,24], which is evidenced by the increased weight of the catalyst after the reaction. During the catalytic decomposition reaction, methane molecules are initially adsorbed (with dissociative adsorption) and decomposed on the metal surface of the catalyst particle, resulting in the formation of chemisorbed carbon species and the release of gaseous hydrogen; the carbon species then dissolve and diffuse through the bulk of the metal particle. Deactivation occurs when the rate of carbon diffusion through the metal catalyst particle is slower than that of the formation of carbon at the surface of the Co0 sites. Under these circumstances, carbon builds up at the catalyst surface and eventually encapsulates the metal particle causing activity loss [8,15,24]. Apparently, there was no formation of cobalt carbide. This is formed from cobalt oxide (CoO), through the decomposition of CH_4 , forming CO and CO_2 , which were not observed during the test.

The 9-Co/ Al_2O_3 catalyst behavior was evaluated through changes in the methane concentration in the efflu-

ent flow, this catalyst being selected due to its performance under the previous reaction conditions. Fig. 5 shows the catalyst behavior with different $N_2:CH_4$ molar ratios. The results showed an increase in the average methane conversion values with an increase in the $N_2:CH_4$ molar ratio. Under a feed flow condition where methane was more diluted, the catalyst gave the highest conversion value (22%). On the other hand, when the methane was very concentrated in the reaction feed flow, that is, using $N_2:CH_4$ in molar ratios of 4:1; 2.5:1 and 1:9, the catalyst gave lower conversion values, not exceeding 12%. This behavior may be due to the amount of active sites present in this catalyst not being sufficient to convert all of the reactive molecules in contact with the catalytic surface because of the increase in the reaction feed flow mixture concentration. In this way, a given amount of reagent would pass through the catalytic bed without undergoing any kind of effective interaction with the catalytic surface, remaining at higher concentrations in the reaction effluent, causing lower methane conversion values.

Moreover, in the tests with a $N_2:CH_4$ molar ratio of 2.5:1, an ongoing catalytic deactivation until a total loss of activity at 200 min of reaction was noted. However, for the catalyst with a $N_2:CH_4$ molar ratio of 1:9, a high initial catalytic activity was observed (60%), followed by a rapid drop in activity, reaching a conversion rate which remained almost constant until the end of the reaction. This is mainly due to the more extreme working conditions where the formation of carbonaceous materials is favored, giving rise to the surface blocking of the active site. However, for the more diluted methane tests, total deactivation of the catalyst was not observed. Under these conditions, CH_4 is more diluted causing carbon deposition to be lower or less favored, thus giving rise to conversion values which remained constant and elevated until the end of reaction.

A stability study was carried out using the 9-Co/ Al_2O_3 catalyst (Fig. 6), since this sample had the best catalytic

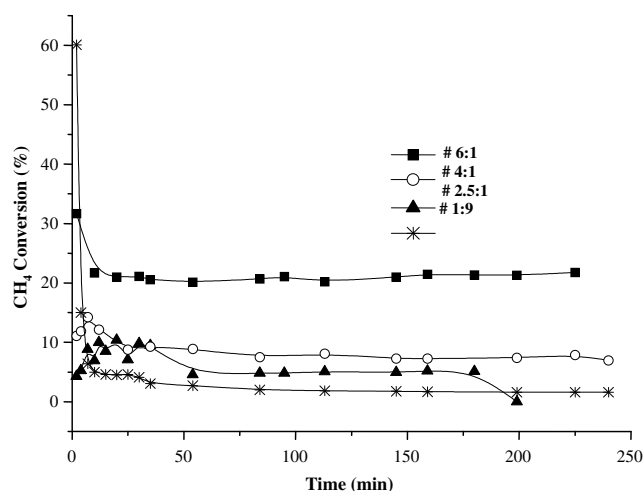


Fig. 5. Methane decomposition over 9-Co/ Al_2O_3 catalysts. Performance of the 9-Co/ Al_2O_3 catalyst in the CH_4 conversion with time-on-stream at 700 °C at different $N_2:CH_4$ molar ratios.

performance. The test was carried out at 700 °C with a $N_2:CH_4$ molar ratio of 6:1, for 450 min.

According to the results, the catalyst remains active for the 450 min of the test, demonstrating that this catalyst is effective in the CH_4 decomposition reaction. In the stability test with the 9-Co/ Al_2O_3 catalyst, the activity remained almost constant throughout the test period. The activity evolved from 35% to 29% with a gradual deactivation revealing the effect of the accumulation of carbonaceous material on the solid surface.

3.3. Sample characterization after catalyst tests

The changes in the surface properties, including pore properties, were measured using the surface images (SEM) for the fresh and used Co/ Al_2O_3 catalysts. Some of the surface properties are summarized in Table 2 and the SEM images are shown in Fig. 7. For almost all catalysts, the BET surface areas were significantly reduced after reaction in the methane stream. For example, the BET surface area of the 9-Co/ Al_2O_3 catalyst, after a reaction at 700 °C, decreased from 252 to 184 $m^2 g^{-1}$. This may be related to this catalyst showing the highest activity during the methane decomposition which led to the greatest decrease in surface area. The pore volume also decreased for this catalyst after the decomposition reaction, from 0.3623 to 0.2560 $cm^3 g^{-1}$. These phenomena result from the carbon deposition, especially in the pores of the Co/ Al_2O_3 catalysts, which contribute greatly to the surface area and pore volume characteristics of Co/ Al_2O_3 catalysts. The rapid deactivation of the catalysts due to carbon deposition is the major problem for hydrogen production using this route. Such undesirable carbon deposition leads to the blocking of the pores and the consequent covering of the active sites. An exception was the 9-Co/ Al_2O_3 catalyst which had a higher surface area and pore volume after the catalytic test with a $N_2:CH_4$ molar ratio of 4:1. It can be

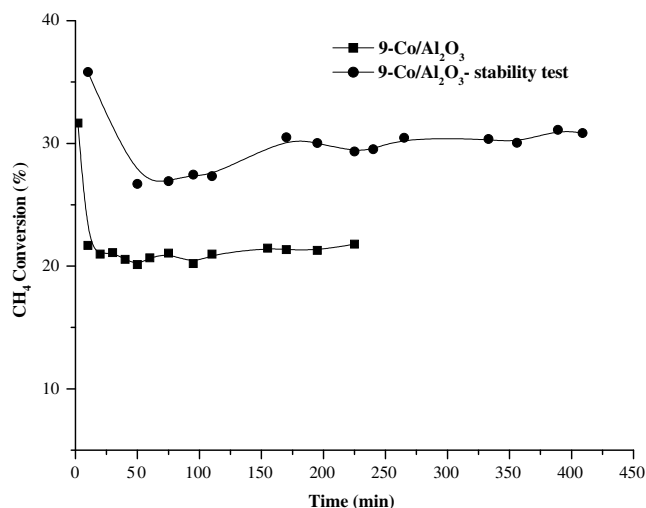


Fig. 6. Methane decomposition over 9-Co/ Al_2O_3 catalyst. Stability study of the catalyst in the CH_4 conversion with time-on-stream at 700 °C and $N_2:CH_4 = 6:1$ molar ratio.

Table 2

Surface property changes of Co/Al₂O₃ catalysts after methane decomposition for 240 min at different reaction temperatures (#) and N₂:CH₄ molar ratio (*)

	2-Co/Al ₂ O ₃	6-Co/Al ₂ O ₃	9-Co/Al ₂ O ₃				
	#800 °C	#800 °C	#800 °C	#700 °C			
	*6:1	*6:1	*6:1	*2.5:1	*4:1	*6:1	*1:9
S_{BET} (m ² g ⁻¹)	199	245	156	201	287	184	137
V_{BJH} (cm ³ g ⁻¹)	0.267	0.387	0.254	0.272	0.405	0.256	0.189

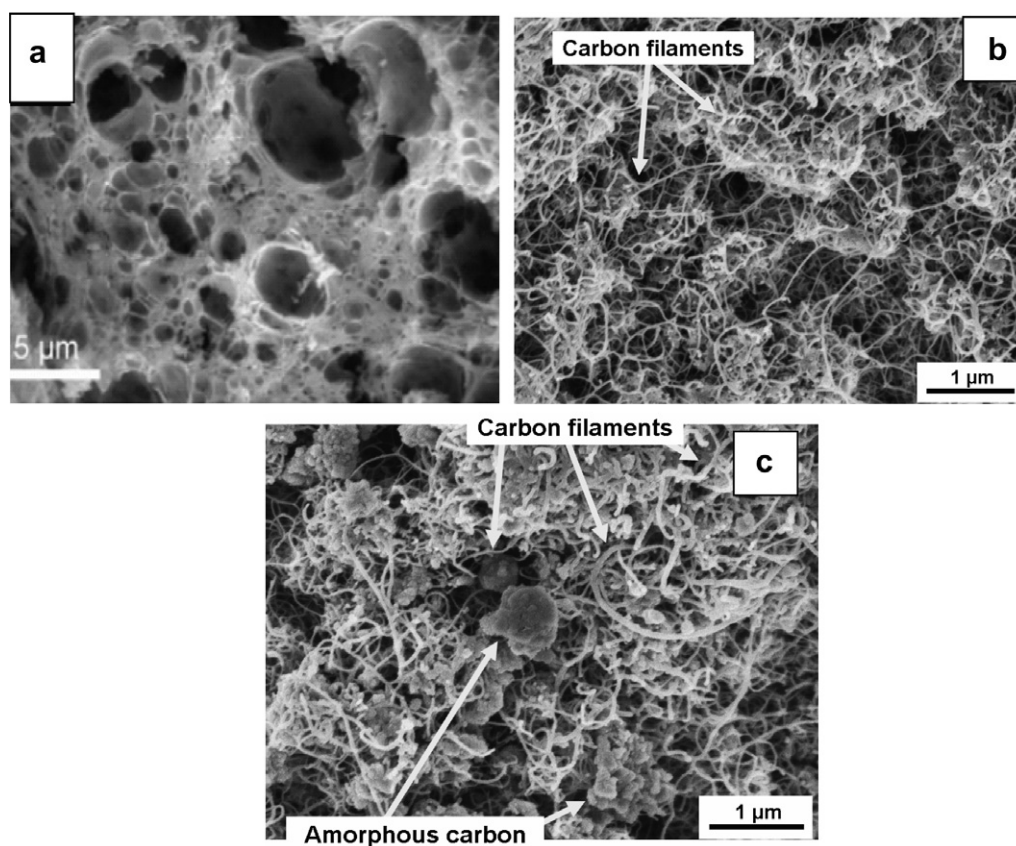


Fig. 7. SEM images of the 9-Co/Al₂O₃ catalyst surfaces: (a) before, (b) N₂:CH₄ 4:1 molar ratio and (c) N₂:CH₄ 6:1 molar ratio, after the CH₄ decomposition reaction.

observed that this behavior is the opposite to that described above, suggesting that the carbon, with a higher surface area, is deposited mainly on the catalyst surface leading to an increase in the final surface area of the catalyst.

These observations are confirmed by the SEM images that show the changes in the surface of the Co/Al₂O₃ samples after the catalyst tests (shown in Fig. 7b and c), where carbon deposition is clearly seen on the sample surface. Also, the carbon produced using the Co/Al₂O₃ catalysts appears to be of different types. Part of the carbon deposition was in the form of carbon filaments or carbon fibers and another part was in an irregular agglomerate form.

4. Conclusions

It was observed that the methodology used in the preparation of Co/Al₂O₃ catalysts led to the obtention of mate-

rials with important properties, such as porous structures and high specific surface areas, for application in catalytic processes, such as decomposition of methane. The results indicated that the Co/Al₂O₃ catalysts were active and stable in relation to the decomposition of methane reaction for the production of hydrogen. This process produces CO/CO₂-free hydrogen in a single step, which is a very attractive feature for application in fuel cells. It was observed that the catalytic performance is dependent on the catalyst characteristics and on the operational conditions employed. The conversion of methane is increased with metal loading, reaction temperature and N₂:CH₄ molar ratio. According to the results, a reaction temperature of 800 °C, a N₂:CH₄ molar ratio of 6:1 and Co loading of 20 wt.% are the best conditions for hydrogen production from the direct decomposition of methane.

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