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Methane steam reforming on supported and non-supported molybdenum carbides

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Abstract

Alumina-supported and non-supported molybdenum carbides were prepared from trioxide of molybdenum for methane steam reforming. The transition metal carbides are formed in a process of carburization, substituting the oxygen by carbon atoms in the crystal lattice of these metals. The samples were carburized at 700 °C, 800 °C and 900 °C. The characterization of solids was performed by elemental analysis, X-ray diffraction, N_2 adsorption and temperature-programmed surface reaction. Catalytic tests were carried through in a fixed-bed quartz micro-reactor and analyzed with on-line gas chromatography. All the catalysts show stability during the reaction. The most actives samples were those carburized at 700 °C, both among the supported and non-supported catalysts. These solids had largest surface areas and the lowest free carbon deposition on the surface, leading to higher H_2 yields than catalysts treated at 800 °C or 900 °C.

Keywords: Methane steam reforming; Molybdenum carbides; Hydrogen generation; Carbon deposition

1. Introduction

Steam reforming is the process of converting hydrocarbons and water at high temperatures into hydrogen or synthesis gas. Methane steam reforming is a well-established commercial process for the production of synthesis gas with a high H_2/CO ratio (reaction (1)), which can be used as a feedstock for ammonia and methanol syntheses, but is not suitable for Fischer–Tropsch synthesis, when a lower H_2/CO ratio is required. Also, hydrogen is an alternative source of energy to the existent fossil fuel. He can be directly burned in a motor of internal combustion or converted to electrical energy in a fuel cell system.

The methane reforming is frequently accomplished by another reaction, named water–gas shift, which consumes a part of the CO formed to produce CO_2 and additional H_2 (reaction (2)).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^{\circ}_{298} = 206\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298} = -41.2\,\text{kJ/mol} \tag{2}$$

The reaction (1) is endothermic and is favored by high temperatures and reduced pressures. In contrast, reaction (2) is lightly exothermic and favored by lower temperatures [1].

Supported noble metals like rhodium and ruthenium can be used to catalyze the methane reforming. These metals are active and catalytically stable against deactivation, but they are expensive and not available in large volumes [3]. The most frequently used commercial catalyst is the α-alumina supported nickel [2]. A problem encountered in using this catalyst is the deactivation caused by coke formation, via methane decomposition and CO disproportionation when the feed composition of the reactor is near stoichiometric. The solution adopted is the feeding of water in great excess to the reactor, which makes possible the removal of the carbon but results in increase of energy consumption.

A promising alternative to the catalysts, in use nowadays, in methane steam reforming is the transition-metal carbide. They show great potential for applications, compared to the noble metals [4,5], and the raw materials used to prepare the carbides, usually metal oxides, are abundant and cheaper.

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The transition metal carbides are formed by substituting the oxygen atoms by carbon atoms in the crystal lattice of these metals. Molybdenum carbide, in particular, is active and stable for hydrocarbon reforming and is resistant to deactivation by poisoning with SO_x, which is present in natural gas, the principal source of commercial methane [4]. Some previous studies have revealed that it can resist deactivation by coking.

Several methods to prepare molybdenum carbides are described in the literature [5–8]. Saito and Anderson [7], obtained carbides of low superficial area (7 m^2/g) from metallic molybdenum and carbon monoxide or using a mixture of methane and hydrogen as carburant. Lee et al. [4], utilizing molybdenum trioxide and carburizing with a high flux of CH_4/H_2 (8 L/h), obtained catalyst with surface areas larger than 18 m^2/g. Other authors [9–11] have prepared molybdenum carbides supported on alumina to improve the surface areas.

In the preparation these materials, in addition to the formation of carbide, it is necessary to check the formation of free carbons. Free carbon is deposited on the solid surface during the metal carburization at high temperatures and is classified as graphitic carbon or as pyrolytic carbon, a pregraphitic form that is not yet very organized. This free carbon may be deposited over the active sites and deactivate the catalyst. To overcome this problem, Sato et al. [6] proposed a temperature-programmed surface reaction (TPSR) with hydrogen, which can remove these carbon species and recover the catalytic activity.

Some authors have reported [7] that molybdenum carbide catalysts are only stable at elevated pressures (8 bar) and that they transform into MoO_2 at ambient pressure. Since steam reforming is conducted at about 30 bar, industrially this might not be a problem. The main problem with the metal carbides has been the difficulty in obtaining materials with sufficiently high surface area for catalytic applications.

This paper is focused on an investigation of the preparation and application of non-supported (Mo_2C) and alumina-supported (Mo_2C/Al_2O_3) in methane steam reforming. An attempt is made to draw conclusions on the influence of temperature on carburization. The carbon accumulated under carburization conditions was measured and studies of stability and selectivity of the catalyst during the reforming reaction and of its property of avoiding the formation of CO_2 through the water–gas shift reaction were performed to evaluate its catalytic properties.

2. Experimental

Mo_2C was prepared by carburization of anhydrous MoO_3 (Mallinckrodt) in a flux of 4 L/h of CH_4/H_2 (20% CH_4:80% H_2 in volume). The reactions were conducted for 180 min at 700 °C, 800 °C or 900 °C, at a heating rate of 10 °C/min. All carburization temperatures were higher than 650 °C because at lower temperatures only molybdenum reduction (Mo^{6+} to Mo^{4+}) occurs [8–11] and the carbide does not form. In the preparation of the supported catalysts, commercial γ-alumina (Degussa) was impregnated with an aqueous solution of ammonium heptamolybdate (99%, Merck) in a rotative evaporator. After the impregnation, the samples were dried at 60 °C for 24 h and then calcined in air (30 mL/min) at 500 °C for 3 h to decompose the precursor and form MoO_3 deposited on γ-alumina (198 m^2/g). Next, the samples were submitted to carburization, following the same method described for non-supported catalysts. The mass loading of molybdenum supported on alumina was of 5%.

A URD-6-Carl Zeiss JENA X-ray diffractometer with Cu Kα radiation was used to identify the crystal phases of the catalysts. The BET surface area of the catalyst samples was measured in Quantachrome NOVA 2000 equipment, with nitrogen as the adsorbate gas. The accumulation of carbonaceous species on the catalyst surface produced during the carburization step was determined by temperature-programmed surface reaction. The methane formed during the TPSR was quantified in a Varian CP-3800 gas chromatograph with TCD detector by passing a mixture of 10% H_2/N_2 over the samples, which were heated from 100 °C to 900 °C at 2 °C/min. The effluent gases were separated by a molecular sieve 13× chromatographic column (3 m × 1/8 in.). The amount of carbon deposited was determined by elemental analysis with a CHNS-O analyzer CE 1110 at 1200 °C. These tests were done to determine the total amount of carbon in the samples after the steps of carburization, TPSR and catalytic tests.

The activity, selectivity and stability measurements of the Mo_2C and Mo_2C/Al_2O_3 catalysts in methane steam reforming were conducted at 1 atm in a conventional flow apparatus. Before the reaction, 127 mg of MoO_3 (non-supported catalyst) and 150 mg of MoO_3/Al_2O_3 (supported catalyst) were carburized at 700 °C, 800 °C or 900 °C by passing a CH_4/H_2 gaseous mixture for 3 h, as described above, and soon afterwards the TPSR was performed, also as described above. After that, the reactor temperature was lowered to 700 °C and the steam reforming reaction conducted. In the reactor apparatus, the water feed was controlled at 6.5 mL/h using a high-pressure pump and the CH_4 flux was maintained at 40 mL/min using a mass–flux controller. The feed molar ratio steam:methane used was 4:1.The water was separated from the reaction effluents in a condensation chamber and the gaseous products were analyzed using a Varian CP 3800 gas chromatograph equipped with two TC detectors. The samples were divided into two aliquots. In the first, hydrogen and methane were analyzed using nitrogen gas as carrier in a packed column 13× molecular-sieve. In the other, methane, carbon monoxide and carbon dioxide were analyzed using helium as carrier and two packed columns – 13X molecular-sieve and Porapaq N – arranged in series. At the end of the catalytic test, the methane and water fluxes were interrupted and the catalyst was cooled with nitrogen and kept for subsequent characterization.

Table 1
Textural characterization of molybdenum carbides

Catalyst	Surface area (m^2/g)
Mo_2C (700 °C)	15.3
Mo_2C (800 °C)	11.7
Mo_2C (900 °C)	9.6
Mo_2C/Al_2O_3 (700 °C)	147.5
Mo_2C/Al_2O_3 (800 °C)	101.4
Mo_2C/Al_2O_3 (900 °C)	79.3

3. Results and discussion

Table 1 shows the specific surface areas of the supported and non-supported molybdenum carbides prepared at 700 °C, 800 °C and 900 °C. The surface areas were determined after the TPSR experiments. The surface areas showed a fall with rising carburization temperature. This effect may be associated with obstruction of pores by the carbon formed during the carburization and with sintering due to the high temperature used in the synthesis [12].

XRD measurements performed on the prepared carbides showed peaks at $2\theta = 34.45°$, 37.14°, 39.68°, 49.90°, 58.50°, 67.30°, 74.43° and 75.80° that can be assigned to the beta-phase of molybdenum carbide (β-Mo_2C), with hexagonal structure [12]. In the samples carburized at 800 °C and 900 °C these peaks are more intense than in those carburized at 700 °C, which may indicate that the formation of crystallites of molybdenum carbides is favored at high temperatures. In Fig. 1, we cannot observe any diffraction peaks corresponding to molybdenum oxide ($2\theta = 23.40°$, 25.50° and 26.75°), indicating that the precursor (MoO_3) was totally transformed, already at 700 °C, to molybdenum carbide during the carburization process.

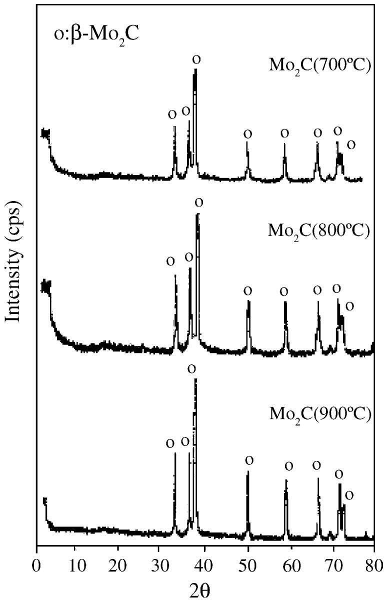

Fig. 1. XRD patterns for the non-supported molybdenum carbides.

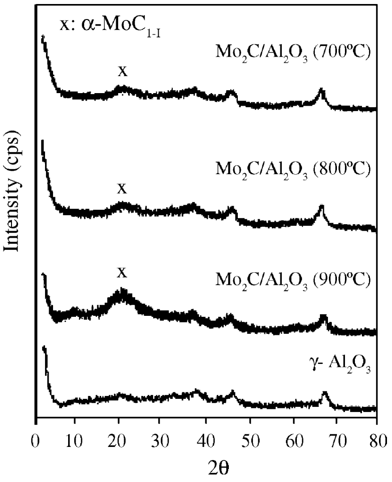

Fig. 2. XRD patterns for the γ-alumina supported molybdenum carbides.

The XRD patterns of the γ-alumina support and of the alumina-supported molybdenum carbides are presented in Fig. 2. It can be seen that, unlike the non-supported samples, the Mo_2C/Al_2O_3 did not exhibit peaks that can be assigned to the phase β-Mo_2C. The peaks at $2\theta = 19.20°$, 37.50°, 45.80°, 67.10° correspond to γ-Al_2O_3. However, it can be seen that the peak at $2\theta = 19.20°$ is more intense that in the standard γ-Al_2O_3. This may indicate the presence of the phase α-MoC_{1-x} ($2\theta = 20.75°$), partially hidden by the γ-Al_2O_3 peak. The small amount of molybdenum (5%, w/w) may also hinder the observation of this supported compound.

During the preparation of the samples, the deposition of free carbon on the catalyst surface may occur. Different kinds of free carbon can be identified by temperature-programmed surface reaction [5], by the formation of CH_4 at different temperatures (reaction) as the reactor temperature is raised. To certify that total reduction of the molybdenum species does not occur during this characterization procedure, after the TPSR the samples was examined by DRX; the Mo_2C spectra remained unaffected, indicating that its total reduction (reaction (4)) did not occur at temperatures below 1000 °C.

$$C + 2H_2 \rightarrow CH_4 \tag{3}$$

$$Mo_2C + 2H_2 \rightarrow Mo + CH_4 \tag{4}$$

Figs. 3 and 4 show that the TPSR profiles of Mo_2C and Mo_2C/Al_2O_3 carburized at 700 °C and 800 °C showed four peaks for methane formation. The first peak, below 300 °C, indicates the desorption step of the methane that remained adsorbed on the catalytic surface after the carburization. The peaks observed between 300 °C and 550 °C can be attributed to formation of CH_4 by carbide carbon. Lee et al. [4] and Myiao et al. [5] observed that a part of the carbide carbon always suffered a small decarburization. The methane formation at higher temperatures was associated with the decomposition of the pyrolytic carbon (550–700 °C) and graphitic carbon (700 °C or higher). The catalysts carburized at 900 °C show only two peaks in the TPSR analysis. The first can be

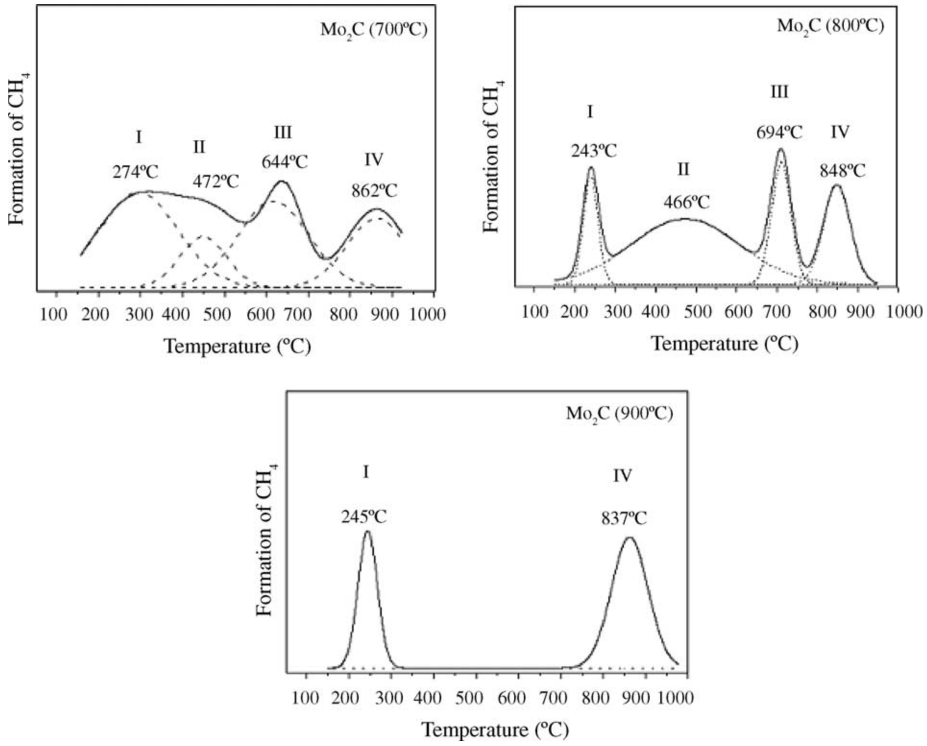

Fig. 3. TPSR profiles of non-supported catalysts.

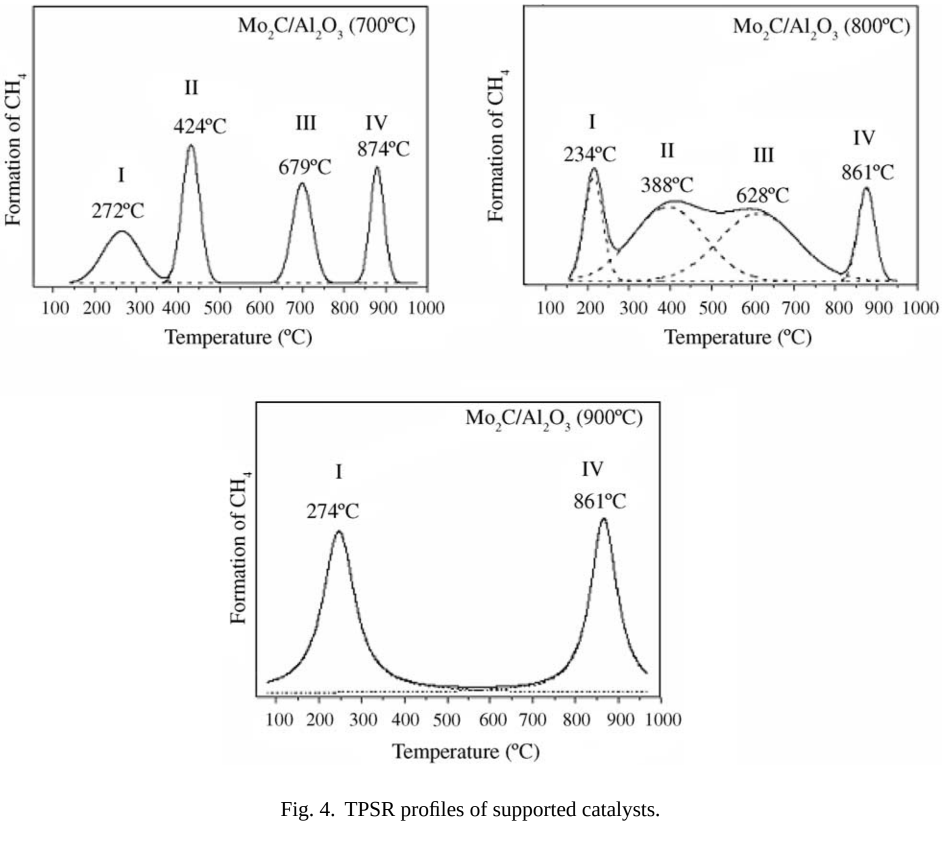

Fig. 4. TPSR profiles of supported catalysts.

Table 2
Carbon associated with the TPSR peaks and carbon mass measured by elemental analysis after carburization and TPSR

Catalyst (3 mg)	Mass of C Peak I (mg)	Mass of C Peak II (mg)	Mass of C Peak III (mg)	Mass of C Peak IV (mg)	Σmass (mg)	$mC_{carb}-mC_{TPSR}$ (mg)
Mo_2C (700 °C)	0.06	0.05	0.05	0.05	0.21	0.22
Mo_2C (800 °C)	0.05	0.12	0.05	0.05	0.27	0.27
Mo_2C (900 °C)	0.18	–	–	0.21	0.39	0.39
Mo_2C/Al_2O_3 (700 °C)	0.01	0.02	0.01	0.01	0.05	0.05
Mo_2C/Al_2O_3 (800 °C)	0.01	0.02	0.02	0.01	0.06	0.07
Mo_2C/Al_2O_3 (900 °C)	0.06	–	–	0.05	0.11	0.11

related to methane desorption and the second to the formation of graphitic carbon, indicating that at this calcination temperature the carbide and pyrolytic carbons were transformed to graphitic.

The measured areas under the peaks represent the hydrogen consumption for CH_4 formation in the carburization reaction and can be used to calculate the number of moles of carbon removed from the catalyst. Table 2 presents the carbon load associated with each peak of the TPSR and the elemental analysis of the carbon remained in the samples after the carburization and TPSR steps.

A comparison of results of elemental analysis with the total carbon load, obtained from the sum of each peak (Table 2), shows that the TPSR results has good acceptance and is in concordance with Lee et al. [4], that suggest the use of the TPSR technique to ‘clean’ the catalyst surfaces and to quantify the carbon content.

The C/Mo relative amounts after the carburization, TPSR and catalytic reaction steps are presented in Table 3. In TPSR, the free carbon is removed from the catalyst surface by reaction with hydrogen (reaction (3)), leaving just the carbide carbon, which is not decarburized (Mo_2C) during the TPSR. After the TPSR, the values of C/Mo for the solids carburized at 700 °C are lower than the theoretical value (0.5), indicating the presence of residual molybdenum oxide. Furthermore, for the solids carburized at 900 °C the C/Mo ratios are higher than the theoretical value, indicating the existence of remained free carbons. After the catalytic tests, the solids carburized at 700 °C presented a C/Mo relation near of the expected by theoretical considerations, indicating the carburization of the residual molybdenum that remained in the oxide state during the methane reforming. These solids showed the best catalytic results. In the other catalysts, in spite of the high values of C/Mo indicate an excess of carbon on the surface, probably as a consequence of carbon deposition by coke formation, any difference was not observed in the methane conversion values.

Table 3
Molar amount of carbon (C/Mo[a]) after carburization, TPSR and catalytic tests

Catalyst	Carburization	RSTP	Catalytic test
Mo_2C (700 °C)	1.34	0.35	0.55
Mo_2C (800 °C)	1.75	0.49	0.71
Mo_2C (900 °C)	2.52	0.67	0.88
Mo_2C/Al_2O_3 (700 °C)	0.84	0.41	0.53
Mo_2C/Al_2O_3 (800 °C)	1.11	0.59	0.75
Mo_2C/Al_2O_3 (900 °C)	1.69	0.78	0.91

[a] Carbon load determined by elemental analysis and molybdenum content determined by ICP.

Figs. 5–7 show the methane conversion and the conversion of methane in products. These conversions were calculated by equations (5) and (6):

$$X_{CH_4} = \frac{F^{\circ}_{CH_4} - F_{CH_4}}{F^{\circ}_{CH_4}} \qquad (5)$$

$$X_{CH_4 \rightarrow \text{product}} = \frac{F_i}{F_{CH_4}} \qquad (6)$$

where, F° and F are the inlet and outlet molar flow.

Fig. 5 shows CH_4 conversion (X) as a function of time on stream at 700 °C, 800 °C and 900 °C over the Mo_2C and Mo_2C/Al_2O_3 catalysts. As shown in this figure, over a test period of 6 h there is no loss of activity on the supported catalysis and only a slight decrease of conversion in the Mo_2C catalyst. In the case of the Mo_2C/Al_2O_3, the conversion is about 45–95%, while for Mo_2C it is lower, around 15–40%. It can be seen that the carburization temperature influenced the conversion level and the catalysts carburized at 700 °C, as a consequence of the higher surface areas, were the most actives. The greater activity of the supported catalysts may be related to the larger activity of the α-MoC_{1-x} species present in Mo_2C/Al_2O_3 samples, compared to the β-Mo_2C species present in Mo_2C or to the higher dispersion of the α-MoC_{1-x} in the supported catalyst. The γ-alumina support is not active in this reaction.

Fig. 6 shows the methane conversion into H_2, CO and CO_2 as a function of time on stream, for the catalysts Mo_2C/Al_2O_3. The hydrogen production varies from 30% to 70%, with the Mo_2C/Al_2O_3 (700 °C) being the most active, followed

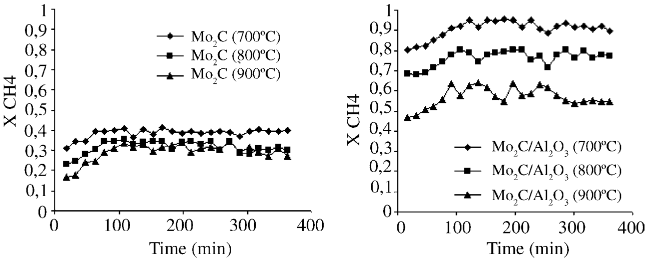

Fig. 5. Methane conversion of the catalysts.

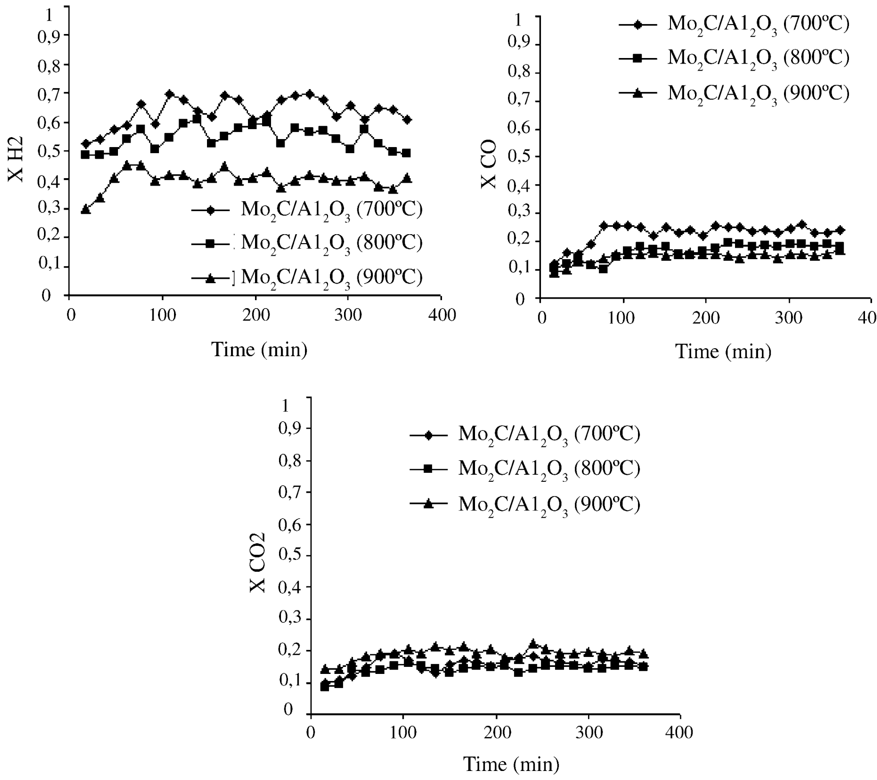

Fig. 6. Products distribution for Mo_2C/Al_2O_3 catalysts.

by Mo_2C/Al_2O_3 (800 °C) and Mo_2C/Al_2O_3 (900 °C). The lower activity produced by Mo_2C/Al_2O_3 (900 °C) is related to the low surface area, to the high formation of graphitic carbon, observed in TPSR, and with the fact that the C/Mo load of this catalyst, after the TPSR step, was higher than the theoretical value, indicating that there was a smaller amount of molybdenum carbide available for reaction.

Fig. 7 shows the products of methane conversion on the Mo_2C catalyst. In this case, carbon dioxide was not formed, indicating that these catalysts are potentially useful for the process of synthesis-gas generation. The most active non-supported catalyst was that carburized at 700 °C, with conversion in hydrogen of 40%. The lower activity of the Mo_2C (900 °C) catalyst may be related to the low surface area and to the direct formation of graphitic carbon that resulted in a lower quantity of carbide, as can be seen in the TPSR.

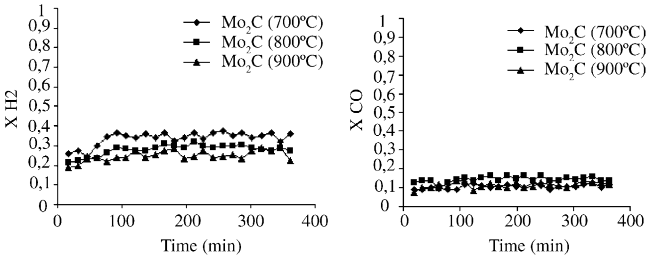

Fig. 7. Products distribution for Mo_2C catalysts.

4. Conclusions

According to the XRD analysis the β-Mo_2C phase appeared only in the non-supported catalysts. In the supported material, the carbide phase is not easily visible, owing to its relatively low content.

TPSR experiments provided evidence of the formation of desorbed carbide carbon and free carbon (pyrolytic and graphitic). Thus, it was crucial, before each assay, to perform TPSR on the catalyst so that it was as active as possible.

Regarding the catalytic tests, all the catalysts proved to be stable throughout the reaction. The most actives samples were those carburized at 700 °C, both among the supported and non-supported catalysts. Although they have very large surface area, this solid had the lowest free carbon deposition on the surface, leading to greater H_2 conversion rates than catalysts treated at 800 °C or 900 °C.

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