



ETHYLENE PRODUCTION BY NATURAL GAS PARTIAL OXIDATION OVER MgO-BASED CATALYSTS

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Abstract. Ethylene industrial production is carried out by steam cracking of naphtha. This process, besides using an oil fraction, requires high energy because it is an endothermic process and takes place at high temperatures. An alternative is the obtainment of this product by partial oxidation of the natural gas. This route, moreover using natural gas as raw material, can be carried out at lower temperatures. Besides, as an exothermic process, the energy produced could be taken advantage for steam production, for example. The catalytic activity runs were carried out over MgO-based catalysts in a tubular quartz reactor heated in an electric oven. The flow rate of gases (methane, air and nitrogen) was adjusted through mass flow controllers. The analysis of the products was carried out in a Varian 3600cx chromatograph equipped with TCD and FID detectors. The experimental data were obtained in the range of 600 to 800°C. Catalysts samples were prepared by a continuous coprecipitation in a CSTR reactor at 60°C, maintaining the pH constant by adjusting the flow rate of solutions. The material precipitated was filtered in vacuum and dried overnight. The oxides were obtained by thermal treatment with synthetic air at 600°C for a period of 6 h. The results show that the main products of the partial oxidation of methane were ethylene and ethane and carbon oxides as by-products. The methane conversion and selectivity to ethylene increase with the reaction temperature and depend on the composition of the catalyst. For temperatures above 700°C, the dehydrogenation of ethane contributes for ethylene production, increasing the ethylene/ethane ratio in the products.

Keywords: Natural Gas, Partial Oxidation, Ethylene Production.

1. Introduction

Ethylene industrial production is carried out by steam cracking of naphtha. This process, besides using an oil fraction, requires high energy because it is an endothermic process and takes place at high temperatures.

An interesting alternative is the ethylene production by partial oxidation of methane that is the main component of the natural gas. This route, moreover using natural gas as raw material, can be carried out at lower temperatures. Besides, as an exothermic process, the energy produced could be taken advantage for other purposes as steam production, for example.

The partial oxidation of methane in order to produce ethylene, denominated oxidative coupling of methane, involves the following partial reactions:



The oxidative coupling of methane has been quite studied in the last decades face to the abundance of the natural gas which is a clean raw material. Krylov (1993) and Lunsford (2000) present a critical review of the achieved progresses. It is known that catalysts with alkaline properties present activity for the oxidative coupling.

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In the works found in the literature on supported catalysts, the main supports used are silica, alumina and oxides of magnesium, zirconium and zinc promoted by alkaline metals as potassium, sodium, lithium and lanthanum (Ahmed and Moffat, 1989; Matsuura et al., 1989; Park and Chang, 1992; Wang et al, 1995; Mallens et al., 1996; Yoon and Tung, 1997; Kim et al, 1997; Yide et al, 1997; Djaidja et al., 2000; Kus et al, 2002). However, in the supported catalysts prepared by impregnation the amount of alkaline metal to be impregnated is limited. To outline this restriction Choudhary et al. (2000) present results with samples of lanthanum and magnesium oxides prepared by mechanical mixture. However, this preparation method has the disadvantage of the resulting sample not to present a uniform composition at molecular level.

In this context the objective of the present work is to evaluate MgO-based catalysts containing lithium or lanthanum prepared by coprecipitation, for the partial oxidation of methane looking for the ethylene production. Besides, also to evaluate the effect of the operation parameters of the reactor such as the composition of the feeding and the spatial velocity.

2. Experimental

The catalysts were prepared by a continuous coprecipitation from solution of nitrates of the metals and solution of NaCO₃ and NaOH as precipitant. The coprecipitation was carried out in a CSTR reactor at 60°C, maintaining the pH constant by adjusting the flow rate of solutions. The material precipitated was washed with deionized water, filtered in vacuum and dried overnight. The oxides were obtained by thermal treatment with synthetic air at 600°C for a period of 6 h.

The catalytic activity runs were carried out in a tubular quartz reactor heated in an electric oven. The flow rate of gases (methane, air and nitrogen) was adjusted through mass flow controllers (Bronkhorst). The analysis of the products was carried out on line in a chromatograph (Varian 3600cx) equipped with TCD and FID detectors and nitrogen as carrier gas. The experimental data were obtained in the temperature range of 600 to 800°C.

3. Results and discussion

Table 1 presents the catalyst samples used in this work, composed by metal oxides of lithium, lanthanum and magnesium, with the respective nominal compositions of the metals.

Table 1. Catalyst samples used in catalytic runs

Sample	Molar content (%)		
	Lithium	Lanthanum	Magnesium
Li15	15	-	85
Li20	20	-	80
Li33	33	-	67
Li50	50	-	50
Li66	66	-	34
Mg100	-	-	100
La5	-	5	95
La10	-	10	90
La20	-	20	80

Two groups of catalysts were used, one group containing lithium and magnesium oxides and other group with lanthanum and magnesium oxides. In reason of the difference in molar weight between lithium and lanthanum metals, the lithium-containing samples were prepared with higher contents. Table 1 also shows the pure magnesium oxide sample denominated as Mg100. To name the other samples, for simplicity was used the content of alkaline metal (lithium or lanthanum) in the sample, once all the samples contain magnesium.

3.1 Lithium-containing catalysts

Figure 1 presents the results of methane conversion into hydrocarbons as function of the reaction temperature for the samples with different lithium contents. For all the samples a significant increase of the conversion is observed up to 750°C. Above this temperature, an appreciable increase of conversion is not observed or a decrease occurs, as in the case of the Li15 and Li33 samples.

Comparing the activity of the different samples, it is noticed that the sample with smaller lithium content (Li15) presents the highest activity, in the whole range of temperature. It is also noted that the larger is the lithium content, the smaller is the conversion of methane. The results of Fig. 1 show that lithium has a doping effect and contents above 15% have a negative effect on magnesium oxide (MgO) activity, possibly decreasing the number of sites of MgO. The alkaline character of lithium increases the basicity of MgO and therefore alters mainly the selectivity.

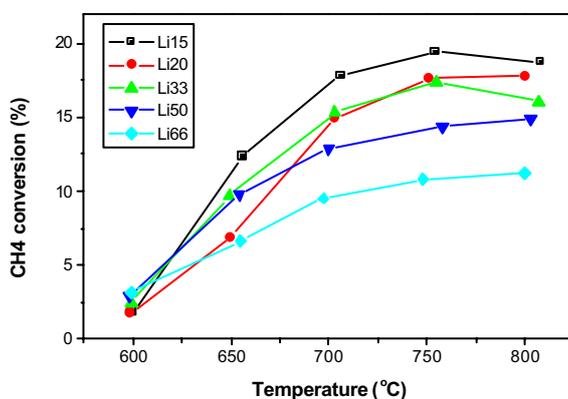


Fig. 1. Methane conversion for lithium-containing samples.

Fig. 2 shows an increase in ethylene/ethane ratio with the reaction temperature. It is also noticed that the two lithium rich samples (Li50 and Li66) present a larger ethylene/ethane ratio and, therefore, larger selectivity to ethylene, mainly at high temperatures, evidencing the role of lithium in the properties of the catalyst.

The data of Fig. 1 and Fig. 2 reveal that lithium influences both the activity and the selectivity of the catalyst. The lithium excess has a negative effect on the activity, however it influences favorably the selectivity. Therefore it is necessary to evaluate both factors to identify the most appropriate sample. Crossing the data of Fig. 1 and Fig. 2 it is verified that the largest yield in ethylene, corresponding to 10.8%, is obtained with the Li15 sample.

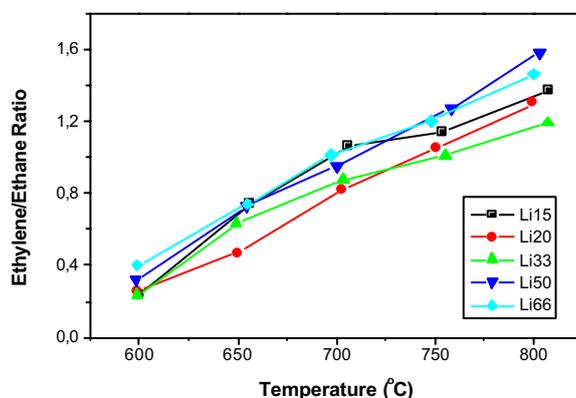


Fig. 2. Ethylene/ethane ratio for lithium-containing samples.

On the other hand, in spite of the results of Fig. 1 have shown that above 750°C there is no increase of the conversion, Fig. 2 shows that in the interval between 750 and 800°C the increase of the ethylene/ethane ratio seems to be still accentuated. This behavior is due to the fact that above 750°C the contribution of the ethane dehydrogenation toward ethylene by equation (3) is more intense, once this reaction is endothermic. Therefore, in this interval of temperature there is an increase in ethylene and decrease in ethane production, resulting in an increasing proportion ethylene/ethane, in agreement with Fig. 2.

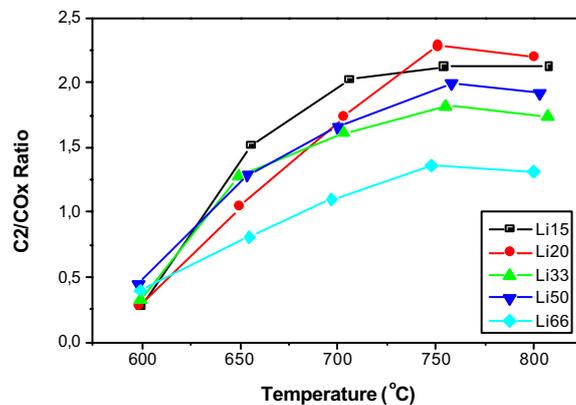


Fig. 3. C₂-hydrocarbons/carbon oxides ratio for lithium-containing samples.

Another important aspect to be considered is the amount of carbon oxides (CO_x) produced in the reaction, once the partial oxidation should form these compounds by methane oxidation or by products (ethylene and ethane) oxidation. Fig. 3 presents the proportion between C₂-hydrocarbons (ethylene and ethane) and carbon oxides (CO_x). This proportion is therefore presented as C₂/CO_x ratio. The results show that the samples with smaller lithium content (Li15 and Li20) present a larger C₂/CO_x ratio compared with the lithium-rich samples. In other words, for smaller lithium contents the production of C₂-hydrocarbons is more intense relative to carbon oxides.

3.2 Lanthanum-containing catalysts

The results obtained for lanthanum-containing samples are presented in Figs. 4 - 6.

Fig. 4 presents the results of methane conversion to hydrocarbons for samples with different lanthanum contents. In this figure it was also included the pure MgO sample, for comparison purposes.

An increase in the conversion is observed with the reaction temperature up to 700°C, except for the sample La20. Above this temperature, increase in the conversion doesn't occur and, in some cases, a drop in the activity takes place as observed for the La20 sample. Comparing the activity of the different samples, it is noticed that the behavior is different depending on the temperature interval considered. For example, at 600°C the samples with larger lanthanum contents (La10 and La20) present larger conversion than the samples with smaller lanthanum contents (La5) or without lanthanum (Mg100). However, for lanthanum-rich samples the increase in activity with the temperature is smaller than for the other samples (La5 and Mg100). In the interval between 700 and 800°C the sample La5 presents evident superiority over the other ones, converging to a conversion value of 20.5%. The other samples tend for a conversion of about 15%, independent of the lanthanum content.

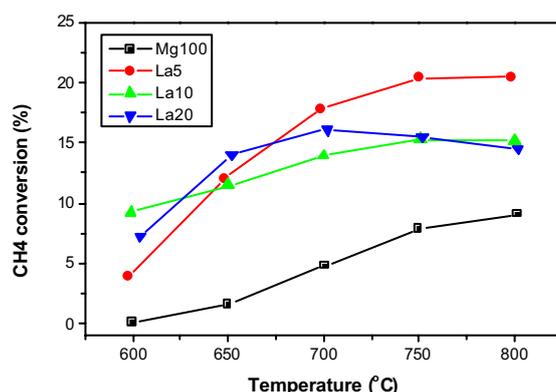


Fig. 4. Methane conversion for lanthanum-containing samples.

The results show, in similar way to the lithium-containing catalysts, that lanthanum has a promoting effect on MgO for oxidative coupling of methane. This positive effect is only obtained for lower contents, in this case 5%, mainly for temperatures above 700°C.

Fig. 5 shows the ethylene/ethane ratio at different reaction temperatures. As it can be seen, this proportion increases with the temperature. For Mg100 sample this increase is linear, while for the lanthanum-containing samples an inflection occurs at 700°C. At temperatures below 700°C the lanthanum-containing samples present larger activity in comparison to the lanthanum-free sample (Mg100), while above this temperature this behavior is inverted. Considering only the lanthanum containing samples, for temperatures below 700°C a smaller ethylene/ethane ratio is obtained for the sample with smaller lanthanum content, while for temperatures above 700°C it is not observed a significant difference for all samples. The results evidence the role of lanthanum in the activity and selectivity for oxidative coupling and this role is strongly related to the reaction temperature.

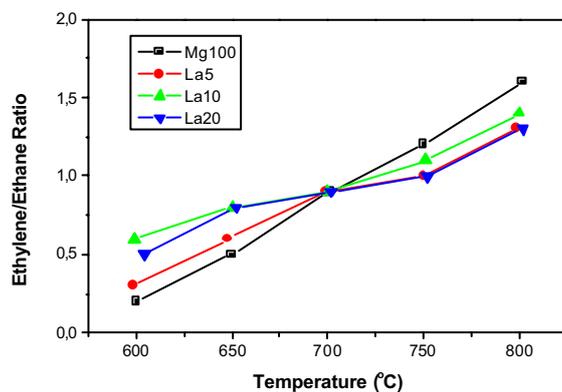


Fig. 5. Ethylene/ethane ratio for lanthanum-containing samples.

With respect to the selectivity toward ethylene given by the ethylene/ethane ratio in Fig. 5, once the ethylene/ethane ratio for the Mg100 sample presents a linear behavior, while the lanthanum-containing samples present different behavior, it can be said that for temperatures below 700°C lanthanum promotes the reaction of partial oxidation of ethane by equation (2) increasing the velocity of this reaction relative to the ethane formation by the equation (1), yielding higher ethylene/ethane ratios compared with the sample without lanthanum (Mg100).

In the interval between 750 and 800°C the behavior described previously for the lithium-containing samples is observed more clearly. In this temperature interval the activity was nearly constant or even decreased (La20), while a greater increase of the ethylene/ethane ratio was observed. This behavior can be attributed to the increase of ethane dehydrogenation rate by equation (3) that is favored with the increase of the reaction temperature, once it is an endothermic reaction. Thus, in this interval ethylene fraction increases at the expense of the ethane produced, increasing the ethylene/ethane ratio, according to Fig. 5.

In Fig. 6 the C_2 -hydrocarbons/carbon oxides ratio (C_2/CO_x) is presented. The results show that the behavior is different depending on the interval of temperature considered, in similar way to the behavior in Figs. 4 and 5. It is interesting to analyze the interval between 750 and 800°C where the largest conversion occurs and at the same time the largest ethylene/ethane ratio is obtained. In this temperature range the proportion C_2/CO_x follows the sequence: La5 > La10 > La20. Consequently, the sample with a suitable lanthanum content is La5, which allows to reduce the carbon oxides production.

On the other hand, comparing the two groups of catalysts, that is, lithium-containing samples and lanthanum-containing samples, and considering the conversion of methane to hydrocarbons and the yield to ethylene (shown by the ethylene/ethane and hydrocarbons/carbon oxides ratios) it can be concluded that the sample that contains 5% of lanthanum (La5) is the one that presents the largest activity and yield of ethylene, among all samples evaluated.

Therefore, the catalyst La5 was later used to verify the influence of the reactor operation parameters such as feed composition and residence time.

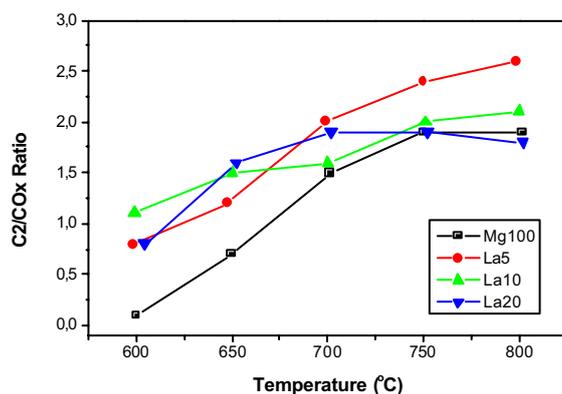


Fig. 6. C₂-hydrocarbons/carbon oxides ratio for lanthanum-containing samples.

3.3 Runs with La5 sample

In Fig. 7 the results obtained at 700°C with different proportions methane/oxygen fed to the reactor are shown. A strong relation is observed between methane conversion and the amount of oxygen fed to the reactor although in this test the flow of methane was maintained constant. It is noticed that for larger amounts of oxygen, that is smaller methane/oxygen ratios, a significant increase in methane conversion is obtained. However, at the same time, a strong decrease of the C₂/CO_x ratio takes place. In other words, the excess of oxygen promotes reactions of methane oxidation to carbon oxides, resulting in an increase in the methane conversion. Therefore, decreasing the amount of fed oxygen, that is, increasing the methane/oxygen ratio, the oxidation reactions are inhibited, thus decreasing the amount of carbon oxides formed.

With regard to the proportion ethylene/ethane, represented as C₂H₄/C₂H₆ in Fig. 7, it is noticed that this amount decreases with increasing CH₄/O₂ ratio in the feeding, showing that the excess of oxygen favors the ethylene production. This result can be explained through the favoring of the ethane dehydrogenation by equation (3), because the oxygen excess in the gas stream would promote the consumption of the hydrogen produced to form water. In other words, in this case the oxidative dehydrogenation of ethane would occur. This result is consistent with the amount of hydrogen produced that remained nearly constant, even taking place an increase of the ethylene/ethane ratio.

The results show that a suitable methane/oxygen ratio exists in order to maximize the production of hydrocarbons and also to optimize the ethylene production. For example, for the conditions presented in Fig. 7, a feeding containing stoichiometric proportion (CH₄/O₂ = 2) produces an ethylene/ethane ratio equal to 1. Increasing the proportion CH₄/O₂ in the feeding decreases the amount of carbon oxides formed, methane conversion and ethylene/ethane ratio.

Fig. 8 presents the results of the run carried out with variable residence time at 700°C and CH₄/O₂=2. The results show that the conversion of methane decreases slightly when increases the residence time, unlike the expected. It is also observed that increasing the residence time the proportion ethylene/ethane decreases that which can be attributed to the oxidation of ethylene to carbon oxides, once the reason C₂/CO_x decreases. In other words, the increase of the residence time increases the production of carbon oxides, because the largest time of contact promotes the ethylene oxidation to these oxides.

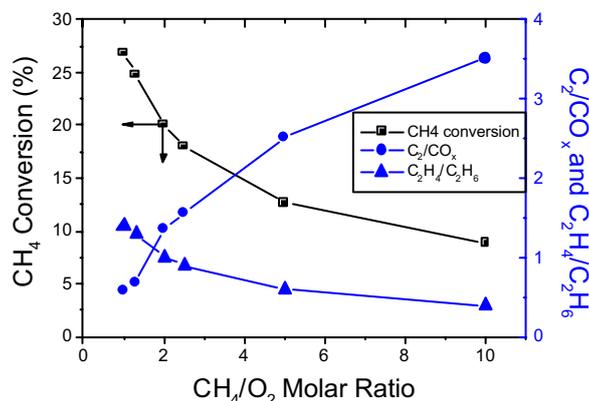


Fig. 7. Influence of CH₄/O₂ ratio fed to the reactor over methane conversion, ethylene/ethane ratio and C₂/CO_x ratio at 700°C.

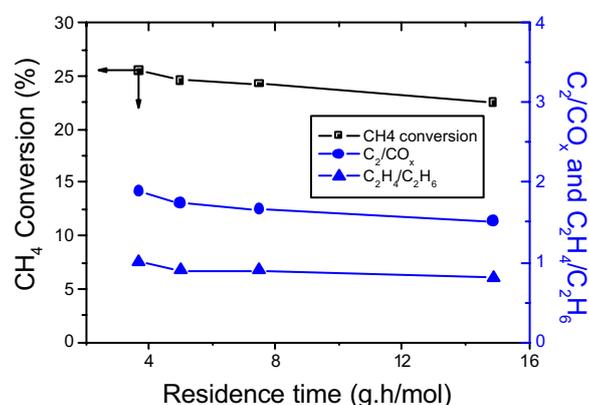


Fig. 8. Influence of residence time on methane conversion, ethylene/ethane ratio and C₂/CO_x ratio at 700°C

Obviously ethane can react with air to form CO₂ by equation (4). However, ethylene react with air through two parallel reactions toward CO and CO₂, equations (5) and (6), respectively, while the two reactions of ethane oxidation are to ethylene (equation 2) and CO₂ (equation 4) formation. Consequently, ethylene has a greater possibility to produce carbon oxides compared with ethane, justifying thus the decrease of the ethylene/ethane ratio and C₂/CO_x ratio with the increase of the time of contact, as illustrated by Fig. 8.



With respect to the decrease in methane conversion with increasing the residence time, this behavior can be attributed to diffusional limitations due to low spatial velocity. This restriction is eliminated by increasing the velocity of the gases as shown in Fig. 8. It is noticed that the oxidative coupling reaction carried out at high spatial velocities, or low times of residence, receives a positive influence in methane conversion as in the selectivity to ethylene besides decreasing the production of carbon oxides. Some authors (Choudhary et al., 2000) also stand out the advantage of the use of high spatial velocities.

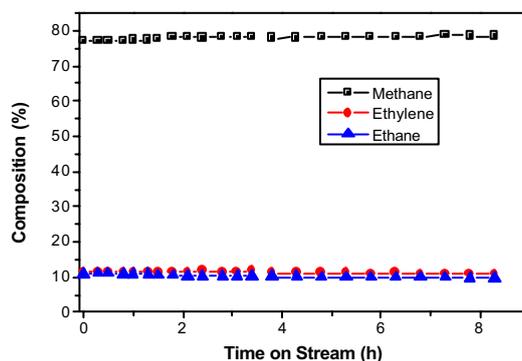


Fig. 9. Composition of hydrocarbons in function of time for reaction over La5 catalyst at 700°C

Fig. 9 shows the results of the run carried out to evaluate the stability of the catalyst. This test was carried out at 700°C with CH₄/O₂ molar ratio equal to 2. The results show that the catalyst maintained an activity practically constant during the whole period of the run, except at the beginning when there was a small variation. The average conversion of methane to hydrocarbons in this period was of 22%. Besides, it is possible to see a slight increase of the ethylene/ethane ratio according to time on stream from 1.0 at the beginning to a value of 1.1 two hours later.

There is no common point of view on the nature of the active sites involved in the oxidative coupling of methane. However, most of the authors came to the conclusion that the active site is surface oxygen. In alkali metal oxide catalysts, it exists as the ionic pair M⁺O⁻ (Krylov, 1991). The active sites involved would be basic sites associated with oxygen vacancies for dissociating gaseous oxygen into atomic species able to activate methane molecules (Lacombe et al., 1994). On the other hand, alkalinity affects the catalyst selectivity by suppressing acid sites and, therefore, inhibiting cracking reactions.

In the case of Li-Mg catalysts, active sites are formed by the substitution of Mg cations in MgO by monovalent lithium and by the formation of defect Li⁺O⁻ (Lunsford, 2002). An excess of Li-containing phase in Mg-based catalysts produces Li₂CO₃ which covers the MgO surface and partially poisons the reaction, in agreement with results shown in Figs. 1-3. On the other hand, the promotion effect of lanthanum can be ascribed to a large increase in the strong basicity of the catalyst because of the doping of MgO by lanthanum, to have in view their alkalinity properties (Kus et al, 2002).

4. Conclusions

The activity and the selectivity to ethylene are strongly related to i) reaction temperature and ii) catalyst composition. The presence of alkaline metal (lithium or lanthanum) in the catalyst has a promoter effect that alters the properties of MgO. The larger the content of alkaline metal in the sample, the smaller the activity and the larger the selectivity to ethylene.

The ethylene/ethane ratio increases with the reaction temperature. For temperatures above 750°C, although the conversion of methane remains constant, the increase in ethylene/ethane ratio is ascribed to an increase in the rate of ethane dehydrogenation.



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From the two groups of catalysts evaluated the samples Li15 and La5 presented greater yield in ethylene. Among these the sample La5 is the one that presents the largest yield in ethylene and smaller production of carbon oxides.

In the runs carried out with the sample La5 it was observed that i) the larger the amount of oxygen fed to the reactor the larger the conversion of methane, the ethylene/ethane ratio and the production of carbon oxides, ii) an increase in the spatial velocity, or decreasing the residence time, increases the conversion of methane and ethylene/ethane ratio and decreases the amount of carbon oxides produced.

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