

Influence of CO₂ on the catalytic performance of La₂O₃/CeO₂ and CaO/CeO₂ catalysts in the oxidative coupling of methane

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In this work the La₂O₃/CeO₂ (33 mol % of La) and CaO/CeO₂ (33 mol % of Ca) catalysts were prepared by the impregnation method and characterized by XRD and CO₂-TPD. The catalytic properties of the catalysts were tested in the OCM process at 1073 K using the methane/oxygen mixture of the mole ratio 3.7 or 2.5 additionally containing CO₂ and helium balance. It was found that in the presence of both catalysts an addition of CO₂ enhances the selectivity to the ethylene and ethane and it does not have any negative influence on methane conversion. In the case of the CaO/CeO₂ catalyst the promoting effect of CO₂ was the highest. When the partial pressure of CO₂ equals to 39 kPa the increase in selectivity from 36 to 41% was noted while the conversion of methane equal to 19.4–19.7 %.

Keywords: CO₂ effect, OCM, lanthanum oxide, calcium oxide, ethylene.

INTRODUCTION

Rich methane resources and their low price motivates to transform this nonreactive molecule into the more useful compounds for the petrochemical industry. One of the basic directions of the research concerning the transformation of the monocarbon compounds is the search for effective direct pathway of methane transformation to higher hydrocarbons.

Researches concerning the oxidative coupling of methane (OCM) process led to a development of a number of catalysts. The significant progress in the research on the OCM process development has been achieved. However, there are still some problems of the economical-technological nature. In the OCM process apart from C₂₊ hydrocarbons a large number of side products, i.e. H₂, H₂O, CO and CO₂ also appears. Usually the yield of C₂ in the OCM process is at the 13–20% level^{1–4}, which is why from the technological point of view the unreacted methane should be removed and returned to the reactor again. Commonly, the presence of even a minor quantity of CO₂ in feed has a negative influence on the properties of the heterogeneous catalyst. More than that, carbon dioxide is not only a side product of this process but also an inseparable component of all the mixtures being the source of methane, irrespective of its origin. Thus, a question arises, is there a necessity of methane purification from the CO₂ before the recycle to the OCM reactor and if so, to what degree?

The aim of the current work was to investigate the influence of the partial pressure of CO₂ on the catalytic performance of the selected basic oxides supported on CeO₂ in the OCM process. Lanthanum and calcium materials were chosen for the research as they are active compounds of many promising active and selective catalysts in OCM^{1–3,5–8}.

EXPERIMENTAL

The catalysts were obtained by the method of impregnation of cerium oxide by water solution of lanthanum nitrate or calcium nitrate. The concentration of the solutions was selected so that after the thermal treatment to obtain the La₂O₃/CeO₂ and CaO/CeO₂ catalysts

containing 33% mol of La and Ca, respectively, which corresponds to the atomic ratio La/Ce and Ca/Ce = 0.5. After impregnation the materials were dried at the temperature of 353 K for 8 h, and then they were calcinated in air flow at 1123 K for 6 h.

The catalytic tests were carried out in the continuous flow quartz reactor with the dimensions (external diameter) x (length) x (wall thickness) = 10 x 270 x 1 mm. Before the beginning of the process the catalyst placed in the reactor was heated in dry helium for 30 min at the temperature of 1123 K. The weight of the catalyst was 400 mg (grain size 0.2–0.3 mm) and the temperature of the process was 1073 K. The reactor was fed by the mixture of the mole ratio CH₄:O₂ = 3.75 which additionally contained helium and carbon dioxide (in the case the process was conducted with CO₂). The partial pressure of CO₂ was controlled by substituting helium with the carbon dioxide, thus the complete volumetric flow rate of the substrates was 156 cm³/min in all the tests. The products of the reaction and unreacted substrates were analyzed using the Agilent 6890N gas chromatograph equipped with two columns (molecular sieve 5A – the analysis of CO and O₂ and Hayesep Q – the analysis of H₂, CO₂, H₂O and hydrocarbons) and the thermal conductivity detectors.

The conversion of methane (α_{CH_4}), yield to ethene and ethane (W_{C_2}) as well as selectivity to product (S_i), i.e. (S_{C_2}) – selectivity to ethane, ethylene, propane and propene, (S_{C_2}) – selectivity to ethane and ethene and S_{CO_x} selectivity to carbon monoxide and dioxide were calculated as described below.

$$\alpha_{CH_4} = \frac{n_{(inlet)CH_4} - n_{(outlet)CH_4}}{n_{(inlet)CH_4}} \cdot 100\%$$

$$S_i = \frac{\sum a_i \cdot n_i}{n_{(inlet)CH_4} - n_{(outlet)CH_4}} \cdot 100\%$$

$$W_{C_2} = \frac{S_{C_2}(\%) \cdot \alpha_{CH_4}(\%)}{100\%}$$

where: $n_{(inlet)CH_4}$ and $n_{(outlet)CH_4}$ are numbers of methane moles in the inlet and outlet of the reactor, respecti-

vely; n_i is a number of products moles in outlet and a_i is a number of carbon atoms in "i" product. In the OCM process carried out in the presence of CO_2 the number of methane moles converted to CO and CO_2 (n_{CO_x}) was calculated assuming the balance of carbon oxides in outlet ($n_{0(\text{outlet})\text{CO}_x}$) and carbon dioxide in inlet ($n_{(\text{inlet})\text{CO}_2}$) of reactor.

$$n_{\text{CO}_x} = n_{(\text{outlet})\text{CO}_x} - n_{(\text{inlet})\text{CO}_2}$$

The analysis of the temperature programmed desorption of carbon dioxide (CO_2 -TPD) was conducted in the quartz micro-reactor using TCD. The weight of the sample used for the analysis was 200 mg. Before measuring the sample was out-gassed at the temperature of 1073 K under a dry helium stream (1 h, $V_{\text{He}} = 30 \text{ cm}^3/\text{min}$). Adsorption of pure CO_2 was carried out at the temperature of 373 K for 0.5 h. The excess of the non-adsorbed CO_2 was removed at the same temperature by flushing the sample with dry helium for 2 h. After that the desorption of CO_2 was carried out using the liner increase of the temperature 10 K/min.

The phase composition of the selected catalysts was determined by the X-ray diffraction technique using the Philips X-PERT device equipped with an X-ray camera ($\text{CuK}\alpha$).

RESULTS

Base physicochemical characterization

Figure 1 presents the powder diffraction patterns obtained for bulk CeO_2 and $\text{La}_2\text{O}_3/\text{CeO}_2$ and CaO/CeO_2 samples. The analysis of the phase composition of pure CeO_2 by the X-ray diffraction method showed the presence of the crystallographic structure typical for the given oxide only. More precisely the reflections observed for pure CeO_2 can be attributed to the typical cubic structure of fluorite type^{9,10}. Similar CeO_2 reflections are observed in the XRD patterns of $\text{La}_2\text{O}_3/\text{CeO}_2$ and CaO/CeO_2 samples. However, the deposition either La or Ca oxides leads to a decrease of an intensity of these reflections. Moreover, in both cases new weak reflections characteristic to hydroxides appeared. The results obtained for $\text{La}_2\text{O}_3/\text{CeO}_2$ correspond to the published data, which show that La_2O_3 is highly hygroscopic and in the presence of humid air converts into lanthanum hydroxide^{11,12}. CaO/CeO_2 catalyst exhibits very similar behavior. In the contact with moisture CaO is converted into the phase of $\text{Ca}(\text{OH})_2$.

Furthermore, in order to investigate the interaction between CO_2 and prepared materials the temperature programmed desorption measurements were carried out. Figure 2 presents the CO_2 -TPD profiles for CeO_2 , $\text{La}_2\text{O}_3/\text{CeO}_2$ and CaO/CeO_2 materials.

In the case of bulk CeO_2 only a single low temperature maximum connected with desorption of the physisorbed CO_2 is present on the TPD- CO_2 profile (the maximum at the temperature ca. 370 K). The profiles of the CO_2 desorption for $\text{La}_2\text{O}_3/\text{CeO}_2$ and CaO/CeO_2 are completely different. In both cases clear maxima of the CO_2 desorption are seen at much higher temperatures. On the CO_2 -TPD profile of $\text{La}_2\text{O}_3/\text{CeO}_2$ two additional maxima of CO_2 desorption, at about 550 and 740 K exist suggesting the presence of medium and strong basic sites, while

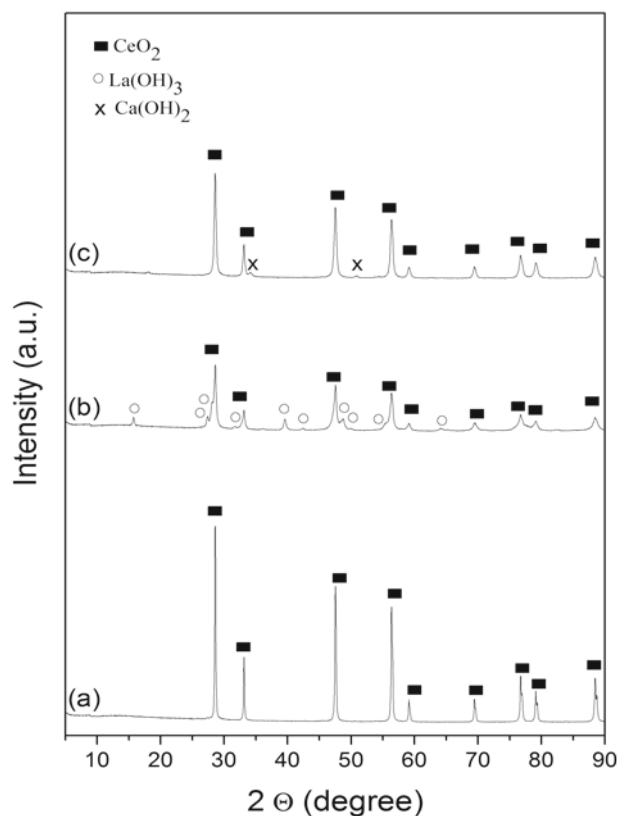


Figure 1. Powder X-ray diffraction patterns of bulk CeO_2 (a), $\text{La}_2\text{O}_3/\text{CeO}_2$ (b) and CaO/CeO_2 (c) materials

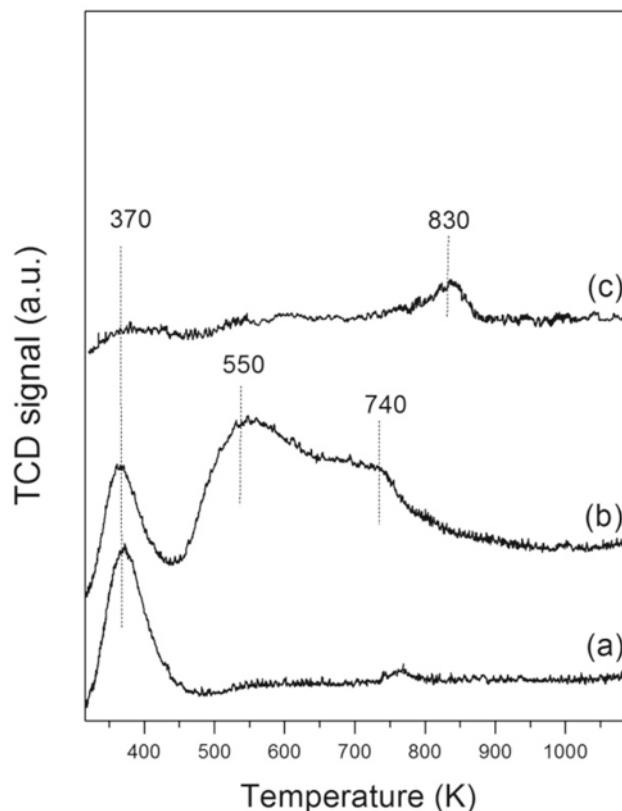


Figure 2. CO_2 -TPD profiles of bulk CeO_2 (a), $\text{La}_2\text{O}_3/\text{CeO}_2$ (b) and CaO/CeO_2 (c) materials

only one high temperature maximum at about 830 K is observed in the case of CaO/CeO_2 indicating presence only strong basic sites. This complies with the published data which show that CaO is characterized by a higher strength of the basic sites in comparison to La_2O_3 ¹³. Summing up, on the basis of the TPD- CO_2 analysis it

Table 1. Catalytic performance of CeO₂, La₂O₃/CeO₂ and CaO/CeO₂ materials in OCM process carried out with and without CO₂ at 1073 K

Sample	Conversion of CH ₄ (%)	Yield (%)	Selectivity (%)			Molar ratio Ethylene/Ethane
			C ₂	C ₃	CO _x	
Blank test	0.9	0.4	44.1	–	55.9	0.2
CeO ₂ ^a	13.2	0.4	3.3	–	96.7	0.3
CeO ₂ ^b	13.7	0.5	3.7	–	96.3	0.4
CaO/CeO ₂ ^a	19.4	7.0	36.1	0.9	63.0	0.6
CaO/CeO ₂ ^b	19.7	8.7	44.2	1.2	54.6	0.6
La ₂ O ₃ /CeO ₂ ^a	18.4	5.6	30.2	0.5	69.3	0.7
La ₂ O ₃ /CeO ₂ ^b	18.2	5.7	31.4	0.4	68.2	0.7

Reaction conditions: $m_{\text{cat}} = 400 \text{ mg}$, $\text{CH}_4:\text{O}_2 = 3.7:1$, $V_{\text{total}} = 156 \text{ cm}^3 \cdot \text{min}^{-1}$, $F/W = 390 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$, $P_{\text{total}} = 0.1 \text{ atm}$.

Results summarized after 15 min-on-stream.

^a process OCM carried out without CO₂; $p_{\text{CO}_2} = 0 \text{ kPa}$.

^b process OCM carried out with CO₂; $p_{\text{CO}_2} = 39 \text{ kPa}$.

can be stated that the deposition either CaO or La₂O₃ on the CeO₂ surface generate basic sites which interact strongly with CO₂.

Effect of CO₂ on catalytic performance in OCM

Table 1 summarizes the catalytic properties of the prepared catalysts in the OCM process carried out with and without CO₂. In all the cases the carbon dioxide additive has a relatively small influence on the methane conversion and the ethylene/ethane mole ratio, while the selectivity to required products of the reaction, i.e. ethylene and ethane (marked as: C₂) increases. Moreover, it can be noticed that CO₂ exerts a higher positive effect on selectivity to C₂ over the CaO/CeO₂ catalyst. In the presence of this catalyst, at the ratio CH₄/O₂ = 3.7 and the pressure $p_{\text{CO}_2} = 39 \text{ kPa}$, selectivity to C₂ increased almost by 8% in comparison to the process carried out without CO₂.

Figure 3 presents the influence of the partial pressure of CO₂ on the conversion of methane, total selectivity to C₂ and C₃ hydrocarbons (marked as: C₂₊) and the ethylene/ethane mole ratio. It is clear that in the case of La₂O₃/CeO₂ an increase of CO₂ partial pressure slightly enhances selectivity to C₂₊ and has very small negative effect on the methane conversion and the molar ratio of ethylene/ethane. In contrast, over CaO/CeO₂ catalyst the selectivity rises clearly with the increase of CO₂ partial pressure. However, the positive effect of CO₂ on the

selectivity to C₂₊ decreases with the increase of oxygen concentration in the feed. For example, over CaO/CeO₂ catalyst when the ratio of CH₄/O₂ in a feed decreases from 3.7 to 2.5 the difference between selectivity to C₂₊ in the process with and without CO₂ drops from 7% to about 4%. This clearly indicates that the effect of CO₂ varies not only with the catalyst properties but also with the feed gas composition.

Assuming that CO₂ exerts the most beneficial changes over the CaO/CeO₂ catalyst in the next stage the influence of time on stream was analyzed using this material. Figure 4 presents the change of methane conversion, selectivity to C₂₊ and the mole ratio of ethylene/ethane with time on stream. In this experiment the composition of substrates was changed periodically (every 150 min).

It is clear that the CaO/CeO₂ catalyst exhibits a high stability during the process carried out for 10 h. The conversion of methane and the mole ratio of ethylene/ethane remained at the same level, while the selectivity to C₂₊ increased clearly each time when carbon dioxide was added to the substrates and decreased when it was removed.

DISCUSSION

The differences in the catalytic properties of tested materials in the process carried out with or without CO₂ are probably connected with the presence of sur-

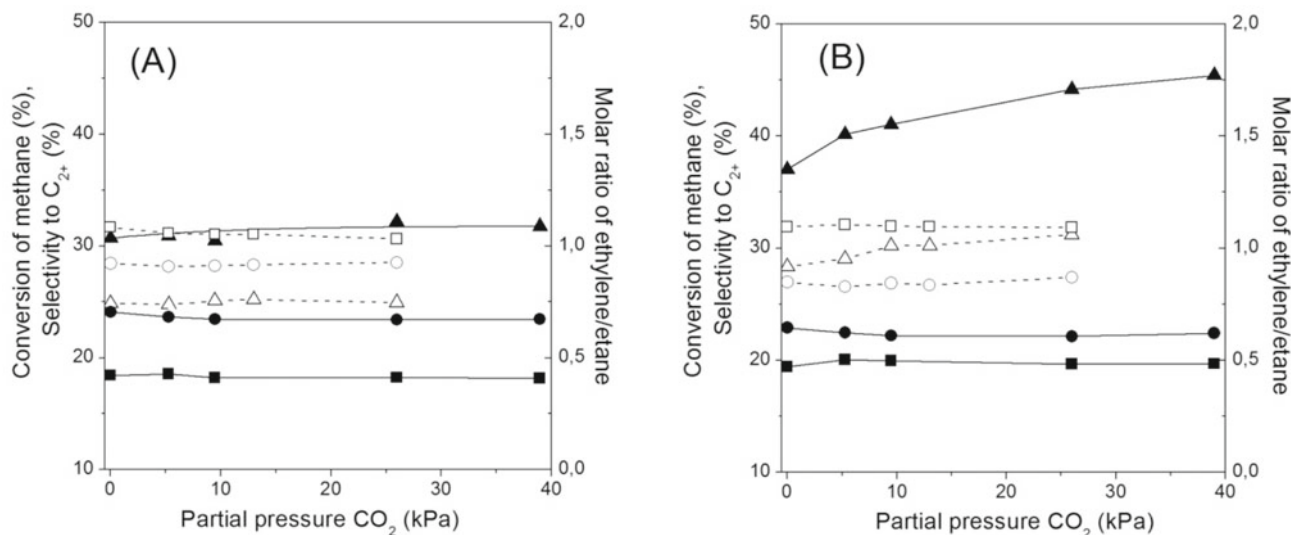


Figure 3. Influence of partial pressure of CO₂ on catalytic performance in OCM at 1073 K over La₂O₃/CeO₂ (A) and CaO/CeO₂ (B) catalysts. Designations: (▲, △) selectivity to C₂₊, (■, □) methane conversion and (●, ○) molar ratio of C₂H₄/C₂H₆. Reaction conditions: $m_{\text{cat}} = 400 \text{ mg}$, $\text{CH}_4:\text{O}_2:\text{X} = (3.7 \text{ or } 2.5):1:4.8$, where: X = He+CO₂, $\text{CH}_4:\text{O}_2 = 2.5$ (open symbols) and $\text{CH}_4:\text{O}_2 = 3.7$ (solid symbols); $V_{\text{total}} = 156 \text{ cm}^3 \cdot \text{min}^{-1}$; $F/W = 390 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$

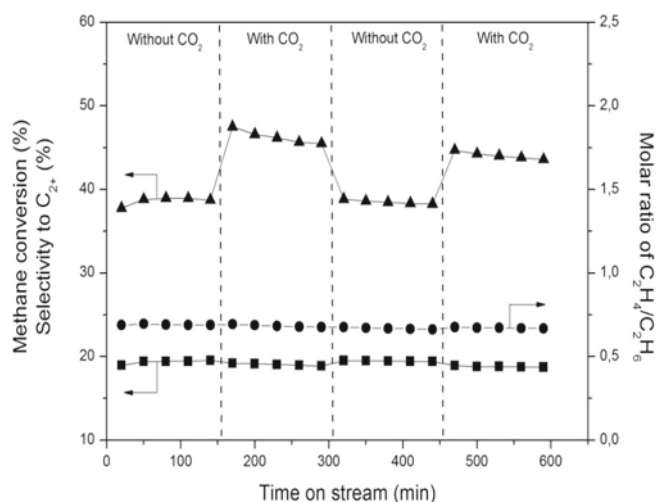


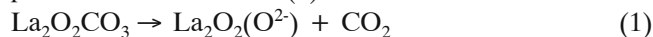
Figure 4. Variation of methane conversion (■), selectivity to C_{2+} (▲) and molar ratio of ethylene/ethane (●) with time on stream at 1073 K over CaO/CeO₂. Reaction conditions: $m_{\text{cat}} = 400$ mg, $V_{\text{total}} = 156$ cm³ · min⁻¹, $F/W = 390$ cm³ · g⁻¹ · min⁻¹. Feed composition: in process with CO₂ CH₄:O₂:He:CO₂ = 3,7:1:4.8:0 and without CH₄:O₂: He:CO₂ = 3.7:1:1.1:3.7

face carbonates. However, the published data are not identical in this respect. In some cases it was found that the presence of carbonates had a negative influence on the catalyst performance in the OCM process. If under the reaction conditions none of the components creates a stable carbonate phase the additive of CO₂ will not have a significant influence on the catalytic performance. The catalysts which were the most sensitive to CO₂ poisoning after the reaction contain a large quantities of the surface carbonates¹⁴. So, the lower temperature of carbonate decomposition making catalyst more resisting to the presence of CO₂ in feed gas. The stable surface carbonates which are not decomposed at the reaction temperature, such as SrCO₃, BaCO₃, are usually seen as agents blocking active centers as they cover the surface by forms of inactive carbonate, which decreases the catalytic activity¹⁴⁻¹⁸.

According to literature data bulk calcium carbonate starts decomposing at the temperature of 693 K¹⁹. In turn, lanthanum carbonate decomposes in two stages. At the first stage, at the temperature of about 753 K La₂(CO₃)₃ decomposes to the intermediate product, La₂O₂CO₃, which may further converts into La₂O₃²⁰. The temperature of La₂O₂CO₃ decompositions varies with the preparation method of catalyst and compositions^{21,22}. Our CO₂-TPD experiments reported in Fig.2 confirms that in the case of La₂O₃/CeO₂ and CaO/CeO₂ catalysts the maxima characteristic for carbonates of Ca and La exist below the temperature at which the OCM process was carried out. Thus probably in these cases CO₂ has insignificant effect on catalytic activity in OCM.

On the other hand, some researchers suggest that the surface carbonates do not only block the active sites but also play an important role in generating the active sites¹⁶. The concentration of the accessible active sites at a given temperature of the reaction depends on the thermal stability of the surface carbonates¹⁶. As a result of decomposing of the surface forms of carbonates the active sites which take part in methane activation can be created and regenerated^{17,22-24}. For instance, decom-

position of La₂O₂CO₃ during the OCM reaction may produce active site O²⁻ (1).



In the present work the decrease of methane conversion and selectivity to C₂₊ was not observed in any cases, on the contrary, at almost constant conversion the selectivity to C₂₊ increased after adding the CO₂ to the feed gas (Fig. 3). Moreover, the positive effect of CO₂ vanishes when CO₂ is absent in the feed mixture (Fig. 4) or it drops with the increase O₂ concentration in the feed. Such results suggest that the effect of CO₂ is probably connected with the adsorption of CO₂ on the sites of total oxidation of methane. The increase of the selectivity to C₂₊ in the presence of CO₂ is often connected with the competitive adsorption^{23,25}. However, in most cases the increase of the selectivity to C₂₊ is usually accompanied by the decrease of methane conversions, which in the case of the analyzed catalysts was not observed. This suggests that over the investigated materials CO₂ is not adsorbed on the sites needed for methane activation. Most probably CO₂ blocks selectively the sites of total oxidation. However, this conclusion needs further experimental investigation.

Finally, it should be pointed that the catalysts containing in their composition cerium, calcium and/or lanthanum oxides are active and selective in the OCM with CO₂ as oxidant (without O₂)^{9,26-29}. Wang and et al.⁹ suggested that the activation of CO₂ takes place on the defects which appeared as a result of doping CeO₂ by calcium ions leading to the appearance of the active forms of the oxygen which take part in methane activation. As was presented in Fig. 3 over both tested catalysts CO₂ exerts an insignificant influence on methane conversion indicating that under reaction conditions, in the presence of a strong oxidant (oxygen) the very weak oxidative abilities of CO₂ are attenuated. However, in our previous investigations we have revealed that over La-containing catalysts in some specific conditions CO₂ may have positive influence on the catalytic activity, too³⁰.

CONCLUSIONS

The catalysts on the basis of rare earth and alkali metals work stably in the OCM process with and without CO₂. Adding CO₂ to the stream of the reagents causes the increase in selectivity to C₂₊ which is clearly seen in the case of the CaO/CeO₂ catalyst. The positive influence of CO₂ on the OCM process is probably caused by selective adsorption on the total oxidation sites. All the components of the catalysts used in the investigation create carbonates which are decomposed at the temperatures lower than the temperature at which the experiment was carried out, so, it is probable that they will not block the active sites permanently.

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