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Simultaneous oxidative coupling of methane and oxidative dehydrogenation of ethane on the Na^+/CaO catalyst

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Abstract

The co-feeding of ethane during oxidative methane coupling (OCM) decreases methane conversion, the more so, the higher the concentration of added ethane. At about 20% ethane content, methane reaction almost ceases. The amount of ethane remaining in post-reaction gases begins to be smaller than that supplied to the reaction only at its concentrations in the methane + ethane + oxygen mixture exceeding 2 mol%. At higher concentrations of ethane fed into the reaction, the magnitude of its conversion becomes stabilized at a constant level of 20–60%, depending on the conditions of the reaction. Along with the rising concentration of added ethane, the carbon contained in methane and ethane undergoing reaction towards the formation of ethylene and hydrocarbons C_{3+} rises, mainly in consequence of the transformations of more highly reactive ethane. Although the presence of ethane among reagents increases ethylene content in post-reaction gases, still the ethylene/ethane ratio in these gases rises only slightly, regardless of the amount of ethane in the initial mixture of methane + ethane + oxygen. A significant finding is the lack of dependence of the value of the conversion of carbon introduced into the reaction in the form of methane and ethane to carbon dioxide on the amount of added ethane, so that the overall selectivity of hydrocarbons C_{2+} formation does not deteriorate, either.

Keywords: Oxidative methane coupling; Oxidative ethane dehydrogenation; Methane conversion; Ethane conversion; Ethylene; Carbon dioxide

1. Introduction

Interest in catalytic oxidative methane coupling (OCM) has already gone through the stage of intensive studies. It has turned out that, it is difficult to obtain satisfactory results with a single pass of the reagents through the catalyst. A method, which allows a considerable improvement of the formation and yield of ethylene obtained from methane in the process of its oxidative coupling, is the application of the re-circulation of unreacted methane after a prior selective adsorptive separation of the products [1–11]. With a properly chosen adsorbent and under optimal conditions of products separation, one of them, ethane, quite quickly ceases to be trapped by the adsorbent and remains in the circulating gases along with unreacted methane. Hence, apart from freshly supplied oxygen and methane, the reaction mixture, which enters the reactor, also contains unadsorbed ethane. Due to it, the whole integrated OCM process includes an additional stage of oxidative ethane dehydrogenation. This reaction takes place in the same reactor, with the same catalyst and under the same conditions as OCM. Both hydrocarbons may then competitively react with oxygen whose amount is limited because of the possibility of self-ignition and explosive hydrocarbons combustion. For that reason, it is important to know the effect of the presence of ethane on OCM. How large is the possible decrease in methane conversion when it competes for oxygen with ethane? Does oxidative ethane dehydrogenation to ethylene in the presence of methane and limited amount of oxygen occur with high effectiveness when the difference in the concentrations of both hydrocarbons is very large on the part of methane? Does not the presence of more highly reactive ethane in the mixture with methane and oxygen cause a significant increase in the formation of carbon dioxide, since it is known that in the case of the reaction with such mixtures most of carbon dioxide derives from ethane oxidation [12–15] ? These and similar questions constituted the reasons for the studies presented.

Experiments concerning separately performed reactions of OCM and oxidative ethane dehydrogenation with catalysts applied in the OCM have been described previously [16–26]. General conclusions of these studies indicate that oxidative ethane dehydrogenation occurs with higher rate, yield and selectivity than OCM. In some papers [16,20], a significantly high participation of homogeneous reactions in

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the process of oxidative ethane dehydrogenation has been suggested. At temperatures above 973 K, this participation may even become dominant. In an empty reactor, without a catalyst, the obtained ethylene yield was higher than in the presence of even the best catalysts, which inhibit homogeneous reactions, possibly by trapping radicals [20].

There were also reports of results of studies on the OCM process in which the reaction mixture contained simultaneously methane and ethane [12–15,27–31]. In the cases when oxidative methane coupling was carried out without a catalyst in the reactor [15,29], the co-feeding of ethane caused an increase in the conversion of oxygen and methane by several times and a considerable increase in the conversion of carbon contained in methane and ethane to ethylene. Ethane underwent reaction more quickly than methane while ethyl radicals, fairly easily formed of ethane, act as initiators for the activation of methane. Similar experiments with the co-feeding of ethane but in the presence of a catalyst yielded an unclear picture of the whole process. In study [15], with the catalyst Sn/Li/MgO, merely a very small rise in the conversion of oxygen was observed with a simultaneous decrease in the conversion of methane. A decrease in the rate of methane conversion on catalyst Sm_2O_3 with ethane added was also reported in study [13]. On the other hand, in studies [28,30] employing catalyst Li/MgO, the authors stated an improvement in reactor performance with ethane in the feed gas—an increase in the conversion of carbon contained in methane and ethane, a rise in the reaction selectivity to unsaturated hydrocarbons, and a decrease of the selectivity to carbon dioxide. In study [31], employing catalyst Na_2WO_4-Mn/SiO_2, it was found out that the presence of methane favours the reaction of oxidative ethane dehydrogenation. Thus, reports on studies with the co-feeding of ethane have not been too numerous, they covered a limited range of reaction conditions and did not concern catalyst Na^+/CaO (which was often employed in the OCM [32–37] and in our studies of the re-circulation process as mentioned [2,4,7–11]), while the conclusions offered in the reported studies have not been unequivocal.

In our studies the concentration of ethane in the reaction mixture was changed in a fairly wide range and the reaction conditions—temperature, oxygen concentration, and contact time—were optimal for the OCM reaction.

2. Experimental

The reaction catalyst was Na^+/CaO, obtained by impregnation of pure calcium carbonate (analytical grade, BDH Chemicals Ltd.) with aqueous solution of sodium carbonate (analytical grade, POCh-Gliwice, Poland) so that the amount of deposited sodium ions was 1.7 wt.%. After water evaporation, the formed paste was dried at 383 K. Dry powder of such catalyst precursor was pelleted and crushed to a grain size of the 0.75–1.2 mm. The catalyst was calcined in pure air (20 cm^3/min) at the temperature 1073 K for 1.5 h just before the beginning of the reaction. Only calcium oxide bulk phase was found, by X-ray diffraction method, after such calcination. The surface area of the catalyst in its oxide form (after calcination), measured by BET method in a static-volumetric apparatus, using argon adsorption at liquid nitrogen temperature, was equal to 2.1 m^2/g.

The reaction of OCM in the presence of ethane, was carried out in a single pass of the reaction mixture through the quartz flow reactor. An internal diameter of the reactor was 10 mm and behind the catalyst layer was narrowing down to 3 mm. Such construction of the reactor enabled a rapid acceleration of the linear rate of gas flow to limit to a minimum the possibility of secondary transformations of the reaction products beyond the catalyst. The amount of the catalyst (W) in the reactor was 0.5 g. The catalyst was mixed with quartz (0.75–1.2 mm grains) at the ratio of 1:10 to warrant the constant temperature in the catalytic layer. The reaction temperature, measured in the centre of the catalyst + quartz bed, was adjusted from 973 to 1073 K. Ethane content in the mixture methane + ethane + oxygen was changed from 0 to 20 mol% and oxygen content from 4.76 to 9.09%. The volumetric rate flow of the reaction mixture (F) was 75 or 150 cm^3/min, and the adjusted contact time (W/F) was 0.4 or 0.2 s g/cm^3.

The analysis of the reaction mixture and the reaction products were performed by means of gas chromatography on Poropak Q (all hydrocarbons and carbon dioxide) using FID and TCD detectors coupled in series, and on molecular sieve 4A + 5A (oxygen) employing TCD detector. In none of the experiments hydrogen and carbon oxide in the reaction products were detected. Chromatographic calibration was carried out with the standard mixtures containing hydrocarbons and other gases, whose concentrations were comparable with those analysed.

The oxygen and methane conversion were calculated on the basis of their concentrations before and after the reaction, with a correction introduced for the change in gas volume during the reaction [38].

In the case of OCM, in the presence of ethane the calculations of the value of the conversion of both hydrocarbons demanded certain formal assumptions. First of all, it has been necessary to assume that ethane introduced into the reaction does not react with methane formation. Such an assumption is based on the literature [13,16,17,20] concerning oxidative ethane dehydrogenation, where it was shown that this assumption is close to truth—the selectivity of methane formation in this reaction is small under most reaction conditions. Small amounts of methane may be products of ethane conversion only at higher concentrations of ethane and at longer contact times [18,20].

The calculation of the degree of ethane conversion, when it was introduced into the reaction along with methane, in the same way as in the case of methane conversion was impossible—ethane present in post-reaction gases constituted not only an unreacted part of the amount of ethane fed into the reactor but it was also a product of the OCM reaction (the differentiation of the origin of ethane in post-reaction gases would require that the studies be performed with methane and ethane contained labelled carbon atoms). Therefore, the value of the degree of ethane conversion was calculated in the following way. The concentration of carbon contained in the reaction products was calculated. Ethane was considered to be a product of the OCM reaction only when its concentration in post-reaction gases was higher than the concentration of supplied ethane—it has been assumed that the concentration of ethane formed in the OCM constitutes a difference between ethane concentrations in post-reaction gases and in the supplied reaction mixture; otherwise, the difference between the concentrations of supplied ethane and that in post-reaction gases constituted a loss of supplied ethane and then ethane was not regarded as a product of the OCM reaction. The difference of thus, calculated concentration of carbon contained in the reaction products and the decrease in the concentration of supplied methane (equivalent to the concentration of carbon contained only in the products of OCM) makes it possible to calculate the concentration of carbon contained in the products formed of ethane and, further, to calculate the degree of its conversion $X_{C_2H_6}$:

$$X_{C_2H_6} = \frac{c_C F - (c^\circ_{CH_4} F^\circ - c_{CH_4} F)}{2c^\circ_{C_2H_6} F^\circ}$$

where $c^\circ_{CH_4}$ is the mole concentration of methane in the reaction mixture, c_{CH_4} the mole concentration of methane in post-reaction gases, $c^\circ_{C_2H_6}$ the mole concentration of ethane in the reaction mixture, c_C the mole concentration of carbon in products present in post-reaction gases, F° the volumetric flow rate of the reaction mixture entering the reactor, F the volumetric flow rate of post-reaction gases.

As has already been mentioned, the determination of the value of the conversion of methane and ethane to particular products and the selectivity of their transformations were impossible because of the unknown origin of hydrocarbons and carbon dioxide formed during the reaction. Only the application of reagents with labelled carbon atoms would make it possible to find out what part of the formed product derives from the conversion of methane or ethane. For that reason, only the overall value of the conversion of carbon contained in methane and ethane introduced into the reaction to particular products x_i was determined, without attempting to specify the origin of a given product from methane or ethane:

$$x_i = \frac{c_i n_i F}{c^\circ_C F^\circ}$$

where c°_C is the mole concentration of carbon ($c^\circ_{CH_4} + 2c^\circ_{C_2H_6}$) in the reaction mixture, c_i the mole concentration of a reaction product "i" in post-reaction gases, n_i the number of carbon atoms in product "i".

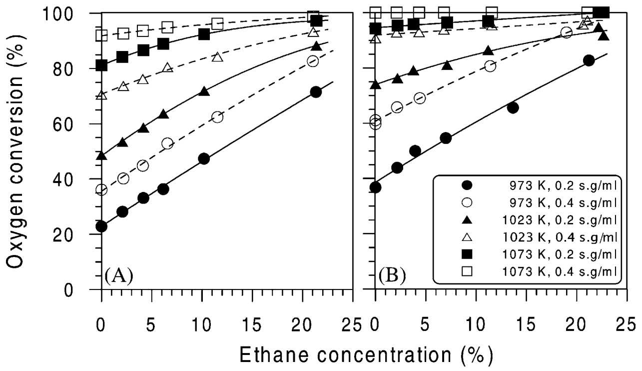

Fig. 1. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of oxygen conversion (oxygen concentration 9.09 vol.% (A) and 4.76 vol.% (B)).

3. Results and discussion

The effect of the presence of ethane in the reaction mixture along with methane and oxygen on the value of oxygen conversion has been shown in Fig. 1. Oxygen conversion was rising along with the rising amount of ethane supplied to the reaction. This is certainly a result of the higher reactivity of ethane whose transformations utilize additional amounts of oxygen, in comparison with OCM alone.

The value of methane conversion (Fig. 2) decreased when the percent content of ethane in the reaction mixture was increased. It is a result of the higher reactivity of ethane, which underwent reaction more quickly than methane (Fig. 3). Our results confirm literature data [13,15]. The fall in the value of methane conversion was higher with rising reaction temperature and lengthened contact times of the reagents with the catalyst. With 20% content of ethane in the reaction mixture the conversion of methane dropped to values close to zero, and in the case of smaller oxygen concentration it even assumed slightly negative values. In that specific reaction conditions, when the content of ethane in the reaction mixture is high, the negative value of methane conversion may be a consequence of the appearance of

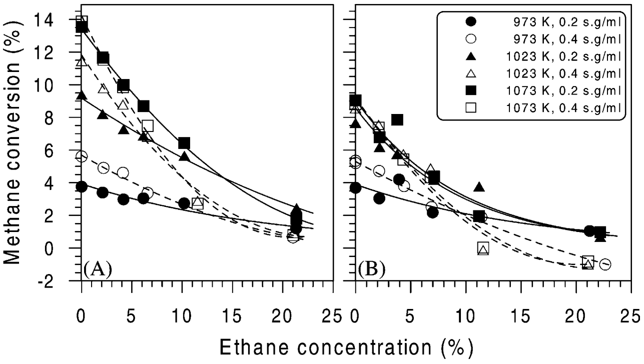

Fig. 2. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of methane conversion (A and B as in Fig. 1).

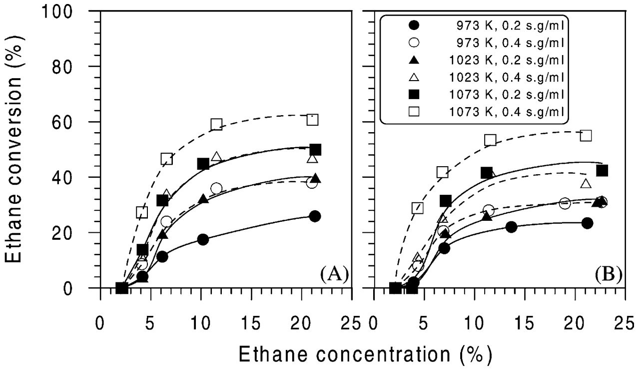

Fig. 3. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of its conversion (A and B as in Fig. 1).

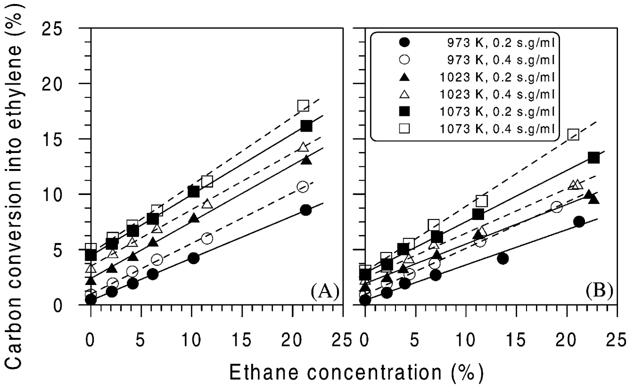

Fig. 4. The effect of ethane concentration in the reaction mixture methane + ethane + oxygene on the value of the conversion of carbon from methane and ethane to ethylene (A and B as in Fig. 1).

additional amounts of methane—significant in this case—derived from the transformation of ethane introduced into the reaction. With the assumed formal assumptions concerning the calculation of methane conversion presented in the experimental part above it, leads to apparently absurd values of the degree of its conversion.

Fig. 3 presents the course of changes in the values of ethane conversion introduced into the reaction along with methane and oxygen. The amount of ethane began to decrease only when its concentration in the reaction mixture exceeded 2 mol%. When its amount introduced into the reaction was smaller—in consequence of simultaneously proceeding oxidative methane coupling whose products also include ethane—ethane concentration in post-reaction gases was higher than in the initial reaction mixture. When the concentration of ethane introduced into the reaction was rising, the value of its conversion quite quickly rose to the level characteristic of given reaction conditions—temperature and contact time. Higher temperatures and longer contact times facilitated higher conversion of introduced ethane. Under the applied reaction conditions the maximum value of ethane conversion reached 60%.

This is an important finding, significant for further attempts at improving the effectiveness of the process of OCM with adsorptive product separation and gases re-circulation. In such a process, it cannot be expected that the whole amount of ethane in circulating gases undergo dehydrogenation to ethylene. Ethane will always be present in circulating gases and its concentration will probably be established on the level determined by the reaction conditions. Another consequence of such behaviour of ethane present in the reaction mixture is a decrease in methane conversion and in the process with gases re-circulation—the necessity of multiplying the number of circulations beyond that indicated only by the OCM effects obtained in the method employing the single-pass mode.

Fig. 4 presents changes in the value of the conversion of carbon fed into the reaction and contained in methane and ethane to ethylene. Carbon conversion to ethylene rose linearly along with the concentration of ethane in the reaction mixture. This is a positive effect for the OCM process with selective adsorptive product separation and re-circulation of unreacted methane together with unadsorbed ethane. It indicates that in such a case the amount of formed ethylene in a single pass of such circulating gases through the reactor with a catalyst is higher than that obtained under the same conditions of the OCM reaction but performed without re-circulation.

With the simultaneous presence of ethane and methane in the reaction mixture, higher reaction temperature and longer contact times facilitated the formation of ethylene. A higher conversion of carbon from both hydrocarbons to ethylene, with a comparable ethane concentration in the reaction mixture, is obtained when more oxygen is supplied for the reaction.

The amount of the conversion of carbon contained in methane and ethane to carbon dioxide is presented in Fig. 5. Although ethane is a more reactive hydrocarbon than methane, its presence among the reagents did not cause the formation of any significantly larger amounts of carbon dioxide than in the case of the reaction mixture containing

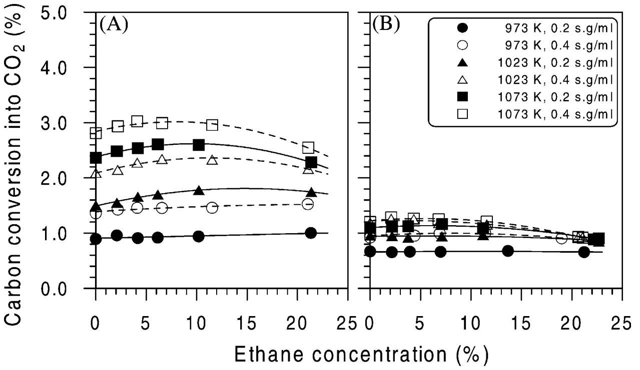

Fig. 5. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of the conversion of carbon contained in methane and ethane to carbon dioxide (A and B as in Fig. 1).

only methane and oxygen (in the diagram, the concentration of added ethane is equal to 0). This is in agreement with the results reported in paper [13] in which, by adding ethane containing carbon ^{13}C, it was found that the total rate of carbon oxides formation of methane and ethane remained unchanged. With a rise in the amount of added ${}^{13}C_2H_6$ there only increased the participation of carbon oxides from this hydrocarbon while that of the oxides from methane decreased. In our studies, with a high, about 20% content of ethane among reagents, even a decrease in the amount of formed carbon dioxide was observed. It may be a consequence of that fact that the lifetime of methyl radicals formed from methane is relatively long and ethyl radicals formed during oxidative dehydrogenation of ethane have much shorter lifetimes [16,18]. There is, therefore, smaller likelihood of further oxidation of ethyl radicals than of methyl radicals and thus the amount of formed carbon dioxide may decrease after substituting ethane for methane in the reaction mixture.

Observations concerning the effect of the presence of ethane on the amount of formed carbon dioxide indicate that—for the OCM process with selective adsorptive product separation and re-circulation of the gases—the intensity of oxidation of hydrocarbons present in the circulating gases does not increase in comparison with that observed during a single pass of the main reagents, methane and oxygen, through the reactor. It is an important indicator because it shows that the presence of ethane does not cause a deterioration of the overall selectivity of the formation of hydrocarbons in the whole integrated re-circulative OCM process. The influence of the main parameters of the reaction—temperature, contact time and oxygen concentration—on the amount of formed carbon dioxide is the same in the case of the reaction mixture methane + ethane + oxygen (Fig. 5) as in that of the mixture methane + oxygen.

The presence of ethane in the reaction mixture together with methane and oxygen contributes to a rise in the amounts of formed hydrocarbons C_{3+}—propylene, propane and hydrocarbons C_4 (Fig. 6), but still carbon conversion from methane and ethane to this group of products was smaller by several times than that to ethylene and carbon dioxide. The increase in the conversion of methane and ethane to hydrocarbons C_{3+} when increasing amounts of ethane were fed into the reaction proves that in the OCM reaction hydrocarbons containing three and more carbon atoms are formed with the participation of dicarbon species (probably radicals) derived from ethane or ethylene.

For the economic effectiveness of the integrated OCM, process with selective adsorptive product separation and re-circulation of methane and ethane, of special importance is the composition of post-reaction gases subjected to adsorption, since it influences the effectiveness of adsorption. It would be desirable that those gases contained the smallest amounts of carbon dioxide and ethane and that the ethylene/ethane ratio would be possibly high. In the light of the above results, ethane content affects the value of methane conversion and the number of re-circulations necessary for total methane utilization. The quantitative composition of the products also affects the manner and costs of their later separation. Since during the OCM reaction ethane is also one of the significant reaction products, for the re-circulation OCM process it is justified here—and for the adaptation of the described results—to treat arbitrarily the overall amount of ethane in post-reaction gases as a product. The distribution of carbon contained in all hydrocarbons higher than methane and in carbon dioxide, included in post-reaction gases, has been shown in Figs. 7–10.

The participation of ethane, formed and unreacted, in the overall amount of hydrocarbons C_{2+} and carbon dioxide is shown in Fig. 7. One may notice here a very slow increase in the amount of ethane in post-reaction gases when raising its concentration in the initial reaction mixture—this increase was more significant when there was less oxygen in the reaction mixture. Only at the temperature of 973 K and contact time equal to 0.2 s g/cm^3 was this increase somewhat quicker already with the addition of a small amount of ethane to the reaction mixture. Thus, incomplete

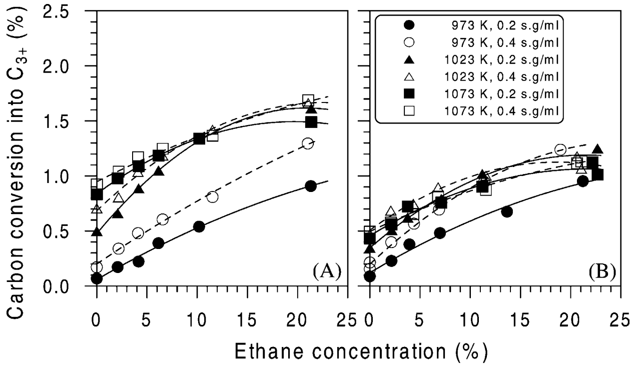

Fig. 6. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of the conversion of carbon contained in methane and ethane to hydrocarbons C_{3+} (A and B as in Fig. 1).

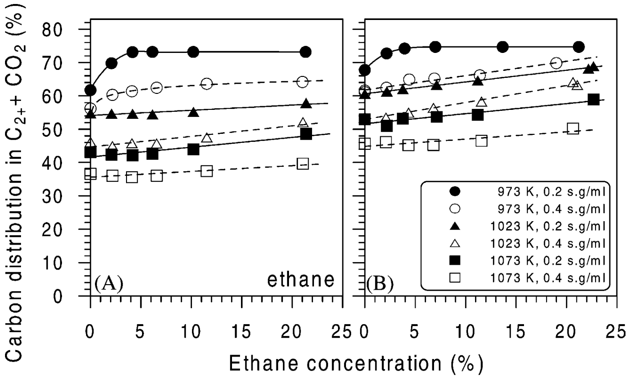

Fig. 7. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the percent participation of ethane in the sum total of hydrocarbons C_{2+} and carbon dioxide in the reaction products (A and B as in Fig. 1).

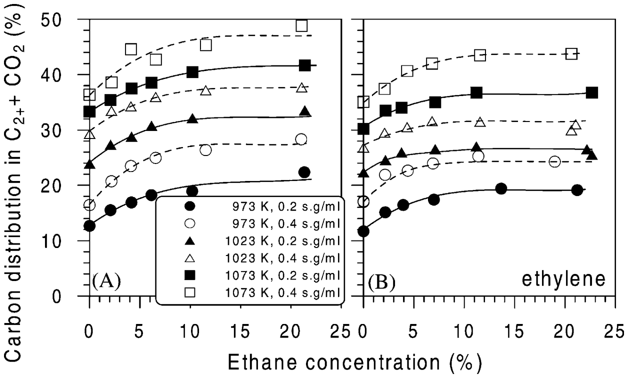

Fig. 8. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the percent participation of ethylene in the sum total of hydrocarbons C_{2+} and carbon dioxide in the reaction products (A and B as in Fig. 1).

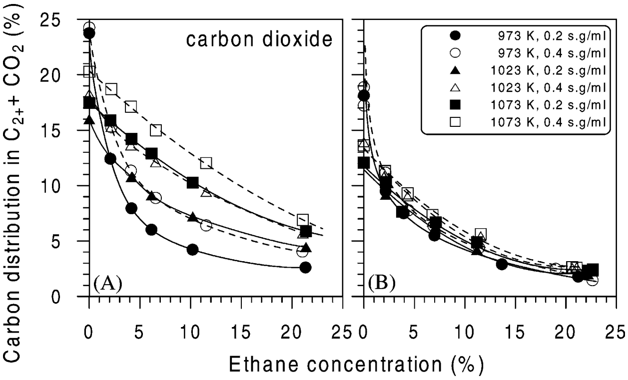

Fig. 10. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the percent participation of carbon dioxide in the sum total of hydrocarbons C_{2+} and carbon dioxide in the reaction products (A and B as in Fig. 1).

conversion of ethane present in the reaction mixture causes an enrichment—luckily only slight—of reaction products with this hydrocarbon. The influence of the conditions of the reaction on the amount of ethane present in post-reaction gases is analogous to that observed in the case of the reaction of methane and oxygen alone. More ethane is there in the post-reaction mixture when the reaction is carried out at lower temperatures, with shorter contact time of the catalyst with the reaction mixture containing less oxygen.

The addition of ethane to the mixture of methane and oxygen also causes an increase in the participation of ethylene among hydrocarbons C_{2+} and carbon dioxide (Fig. 8). For the integrated re-circulation OCM process, it is a desirable and advantageous direction of changes in the quantitative composition of products subjected to adsorption. This increase was quickest in the range of small amounts of added ethane and at higher oxygen concentrations in the reaction mixture. In the range of added ethane concentrations exceeding about 5 mol%, the rate of the increase in ethane participation in post-reaction gases considerable decreased or its content was even stabilized in the case when oxygen concentration was smaller, 4.76 mol%. The effect of the reaction conditions on the level of ethylene participation in post-reaction gases was reversed in comparison with the case of ethane but, similarly to the latter—the same as in the reaction of methane and oxygen alone. More ethylene is obtained at higher temperatures of the reaction, applying a reaction mixture containing more oxygen and with longer contact times with the catalyst.

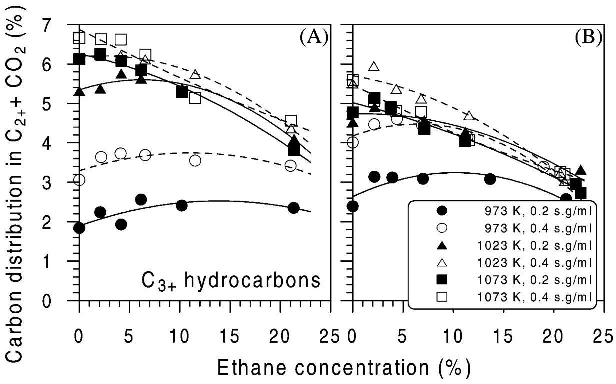

Fig. 9. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the percent participation of hydrocarbons C_{3+} in the sum total of hydrocarbons C_{2+} and carbon dioxide in the reaction products (A and B as in Fig. 1).

The participation of hydrocarbons C_{3+} in reaction products decreased when there was ethane in the reaction mixture; the fall was deeper along with the rising concentration of added ethane (Fig. 9). Only at small amounts of added ethane and at the temperature of 973 K was the influence of the concentration of added ethane small.

The effect of ethane added to the reaction mixture was most evident in the percent participation of carbon dioxide in post-reaction gases (Fig. 10). Even a small concentration of added ethane caused a quick drop in the content of carbon dioxide among the reaction products. The drop was greatest at the lowest temperature of the reaction. An inhibition of the rate of the decrease of the participation of carbon dioxide in the products occurred only at added ethane concentrations higher than about 10 mol%.

The results shown in Figs. 7–10 show that in the re-circulation OCM process with selective adsorptive product separation the composition of post-reaction gases is different than that of the process carried out only with a single pass of the reagents through the catalyst under the same reaction conditions. First of all, post-reaction gases subjected to adsorption contain more ethylene, less carbon dioxide and hydrocarbons C_{3+}. For the effectiveness of the adsorption process, of particular significance is the increase in ethylene concentration with a simultaneous decrease in the concentrations of carbon dioxide and hydrocarbons C_{3+}, because the adsorption of these products is competitive—all the products undergo adsorption on the same sites of the adsorbent. Such changes in the participation of these

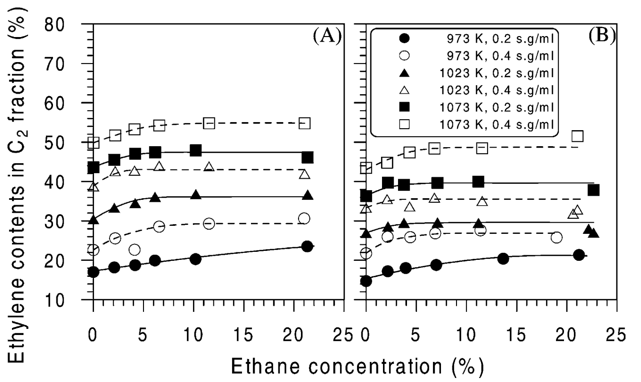

Fig. 11. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the percent content of ethylene in the sum total of hydrocarbons C_2 in the reaction products (A and B as in Fig. 1).

products in post-reaction gases may favourably affect an increase of the effective sorption capacity of the adsorbent in relation to ethylene.

The higher increase in the percent participation of ethylene in post-reaction gases than that of ethane, caused by the presence of the latter in the reaction mixture, has a positive effect on the obtained composition of the C_2 fraction. The percent content of ethylene among hydrocarbons C_2 (Fig. 11) and the ratio between the amounts of ethylene and ethane present in post-reaction gases (Fig. 12) were higher under most reaction conditions than in the products of oxidative methane coupling with a reaction mixture consisting only of methane and oxygen. However, it is not a very significant enrichment of this fraction with ethylene and relatively little dependent on ethane concentration in the reaction mixture. It indicates that during a single occurrence of the reaction of oxidative methane coupling and oxidative dehydrogenation of ethane there is established a state of balance between the concentrations of ethylene and ethane. This balance depends primarily on the reaction conditions—temperature, oxygen content in the reaction mixture and its contact time with the catalyst. More ethylene is formed at higher temperatures, at higher oxygen concentration and longer contact times.

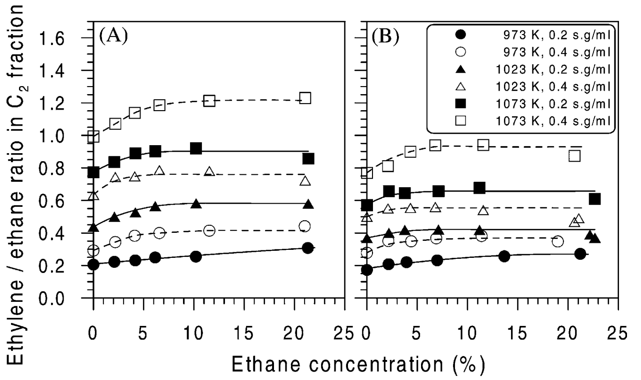

Fig. 12. The effect of ethane concentration in the reaction mixture methane + ethane + oxygen on the value of the ratio of ethylene and ethane in the reaction products (A and B as in Fig. 1).

4. Conclusions

The presence of ethane during oxidative methane coupling affects the amount of methane conversion decreasing it the more, the more ethane is there in the reaction mixture. With about 20% content of ethane, the reaction of methane almost ceases. For the circulation OCM process with selective adsorptive product separation it means that for the total methane conversion the number of re-circulation must be greater than the OCM effects obtained in the single-pass process of the reagents through the catalyst would indicate. Additionally, in order to maintain constant overall pressure in the re-circulation process, after the breakthrough of the temporarily working adsorbent by ethane, the amount of fresh methane fed to the reactor would have to be decreased in comparison with the initial period of the cycle of adsorption.

The amount of ethane remaining in post-reaction gases begins to be smaller than that supplied for the reaction only at its concentrations in the methane + ethane + oxygen mixture above 2 mol%. At higher concentrations of ethane supplied for the reaction the amount of its conversion begins to stabilize on a constant level of 20–60%, depending on the reaction conditions. In the integrated re-circulation OCM process with selective adsorptive product separation, after a quick breakthrough of the adsorbent by ethane, the latter will always be present in circulating gases.

With an increase in the concentration of added ethane, the conversion of carbon from methane and ethane towards the formation of ethylene and hydrocarbons C_{3+} increased, mainly as a result of the conversion of more highly reactive ethane. Ethylene, formed in consequence of the dehydrogenation of ethane fed into the reactor, obviously contributes to a rise of its efficiency in the whole integrated re-circulation OCM process. Although the presence of ethane among the reagents increases the content of ethylene among reaction products, still, due to the established balance between these hydrocarbons, the mutual ratio of the concentrations of ethylene and ethane in these gases, subjected to adsorption later on, increases only slightly, regardless of the amount of ethane in the initial mixture methane + ethane + oxygen.

A very important and significant finding of the reported studies is the lack of dependence of the value of the conversion of carbon introduced into the reaction in the forms of methane and ethane to carbon dioxide on the amount of added ethane. It implies that in the re-circulation OCM process there should be formed no more carbon dioxide than in the reaction of methane and oxygen alone during their single pass through the reactor and that the overall selectivity of the formation of hydrocarbons C_{2+} does not deteriorate, either.

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