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Oxidation of methane–ethane mixtures into alcohols under enhanced pressures

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Abstract

Experimental investigation of the direct partial oxidation of methane–ethane mixtures into alcohols in the pressure range from 2 to 15 atm and at 100 atm was carried out and compared with the results of kinetic simulation of this process. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Methane; Ethane; Methanol; Ethanol; Alcohols

1. Introduction

The process of the direct oxidation of methane to methanol (DMTM) is one of the most promising routes of solving the problem of the conversion of natural gas into more convenient feedstocks and chemicals [1,2]. However, this process needs pressures up to 100 atm, and the conversion of natural gas usually does not exceed 3–5% per pass through reactor [2]. The main product is methanol which does not form stable mixtures with gasoline if its concentration exceeds several percents. Heavier alcohols (ethanol, butanol, etc.) have no such drawback and may be produced by oxidation of the corresponding hydrocarbons with much higher yields and at noticeably milder conditions. So, to enhance the process profitability and to produce more convenient octane components for motor fuels, it is preferable to use in the process hydrocarbon gases with high content of heavier homologous of methane, first of all, ethane. Experimental data available in literature [2] leads us to expect an essential decrease in operating pressure (up to ~30 atm) and temperature (approximately about 100°C) together with the rise of hydrocarbon conversion and economic efficiency for gases with ethane admixture higher than 5%. Thus obtained mixtures of alcohols with higher content of ethanol form more stable mixtures with gasoline. Russia possesses huge and practically unused resources of ethane natural gases. The lack of experimental data on direct ethane oxidation and practical absence of such data for oxidation of alkane mixtures induced this investigation.

Experimental results of this study were compared with the kinetic simulation of the process that were done on the basis of kinetic models used in our previous studies, for example [3,4]. The description

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of the concrete model used in these simulations will be given elsewhere [5].

2. Experimental

The main part of the experiment was carried out in a heated stainless steel flow reactor (i.d. 10 mm, operating part 100 mm, inserted quartz liner i.d. 7 mm) described in [6]. It provides the heating and mixing of separately introduced hydrocarbon gas and oxygen at a time that does not exceed 10% of the total residence time. Output gases were rapidly cooled to ≈150°C and analyzed by online GC. The concentration of ethane was varied from 0% to 100%, and that of oxygen from 2% to 8%. Pressure was changed from 2 to 15 atm at temperatures from 350°C to 500°C and residence time t_{res}=10–50 s. "Chemical pure" grade gases from cylinders were used.

A separate set of experiments at pressure P=100 atm was carried out on a pilot installation used earlier for methane oxidation [7]. In this set ethane concentration was varied from 0% to 22%, that of oxygen – from 2.7% to 3.0% (oxidizing agent – air), and temperature was 350°C.

3. Results and discussion

First of all it is necessary to note the very narrow temperature gap between the temperature at the beginning of the reaction and that of the full consumption of oxygen. This gap does not exceed 10–20°C (Fig. 1). We observed similar behavior in the oxidation of pure methane [6]. The theoretical explanation of this feature of partial oxidation of alkanes involves the existence of two different stable states of the process with very high differences in rates of oxidation and very sharp transition between them [6]. Experimental values of the temperature at the beginning of the reaction slightly exceed the theoretical figures mainly due to the difficulty in the precise determination of this parameter.

The most prominent effect of admixing of higher alkanes to oxidizing methane is the reduction in the temperature of the process [2]. Fig. 1 shows a sharp dependence of this parameter from ethane concentration. The rise of ethane concentration up to 30% reduces the reaction temperature to 360°C, i.e. leads to a drop of ≈100°C against the temperature of oxidation of pure methane. Further rise in ethane concentration leads only to a slight change in temperature.

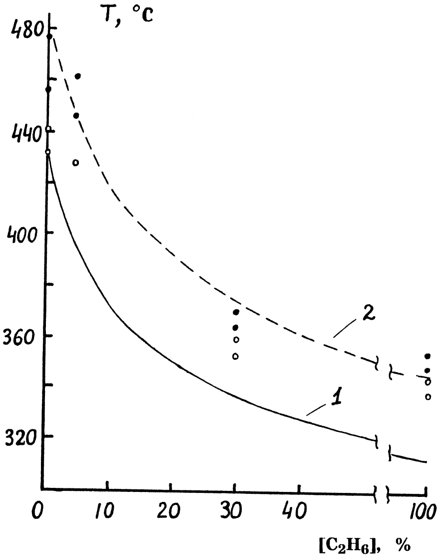

Fig. 1. Effect of ethane concentration on temperature at the beginning of reaction (● and (1)) and temperature of complete conversion of oxygen (○ and (2)). $[O_2]_0$=4.5%, P=10 atm, t_{res}=25 s. Points – experimental data; curves – results of simulation.

The rise of ethane concentration in mixture almost doubles the selectivity of methanol formation and leads to a more significant amount of ethanol in products (Fig. 2). The most prominent changes also occur when concentration of ethane is enhanced from 0% to 20–30%. (In this work for the sake of exactness we use the value $S^{X}_{O_2}$ – the selectivity of formation of product X against the amount of consumed oxygen which is very close to 100%.) Calculations describe this dependence well enough showing flat maximum in the vicinity of $[C_2H_6]_0$=30%.

The variation of oxygen content in the mixture turned out to influence the temperature at the beginning of the reaction and the temperature of the complete consumption of oxygen. For the mixture containing 30% of ethane the increase in the initial oxygen concentration from 2.2% to 6.6% elevates these temperatures from 356°C to 368°C and from 367°C to 375°C, respectively. It confirms our previous

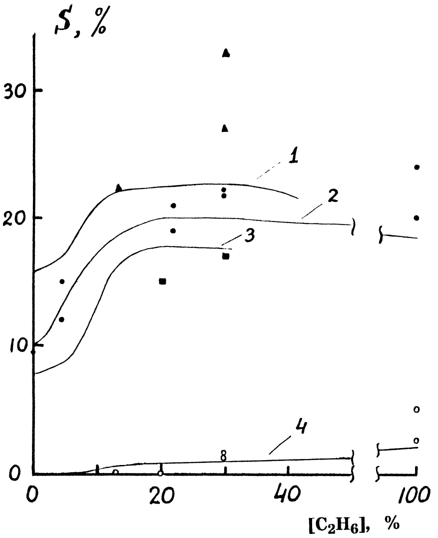

Fig. 2. Effect of ethane concentration on the selectivity of methanol $S_{O_2}^{MeOH}$ (1–3) and ethanol $S_{O_2}^{EtOH}$ (4) formation. P=10 atm, t_{res}=25 s; (▲ and (1)) – $[O_2]_0$=2.2%; (●, ○ and (2), (4)) – $[O_2]_0$=4.5%; (■ and (3)) – $[O_2]_0$=6.5%. Points – experimental data; solid lines – results of simulation.

Table 1
Experimental values of the selectivity of methanol formation $S_{O_2}^{MeOH}$ and methanol yield ($[C_2H_6]_0$=30%; P=10 atm, t_{res}=25 s)

Concentration of oxygen $[O_2]_0$ (%)	Selectivity of methanol formation $S_{O_2}^{MeOH}$ (%)	Yield of methanol (vol%)
2.2	33	1.5
3.0	27	1.6
4.5	22	2.0
6.6	17	2.2
10.0	~5	1.0

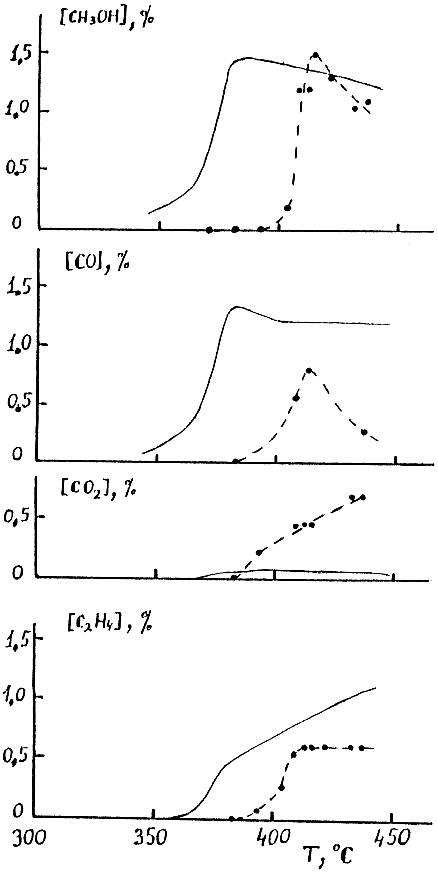

Fig. 3. Effect of temperature on formation of products (vol% in gas flow). $[C_2H_6]_0$=30%; $[O_2]_0$=3.5%; P=10 atm, t_{res} =25 s. Points and dotted lines – experimental data; solid lines – results of simulation.

and on the first site paradoxical theoretical conclusion that at high pressures there exists a range of oxygen concentrations in which the increase of oxygen content inhibits the rate of the process [3]. It also confirms experimental evidences of the elevation of the temperature of the reaction of methane oxidation with the increase in the initial oxygen concentration [6].

Experimental (Table 1) and calculated dependencies of the selectivity of methanol formation $S_{O_2}^{MeOH}$ against the initial oxygen concentration shows a less sharp drop of this selectivity with the rise in oxygen content in comparison with the oxidation of pure methane. It leads to a rise in the methanol yield up to oxygen concentrations $[O_2]_0$=7%, while in methane oxidation such a drop in selectivity is observed at $[O_2]_0$<5% [3]. Significant discrepancy between experiment and calculations is observed only for the low concentrations $[O_2]_0 \leq 3\%$.

Kinetic simulation describes well enough the yield of methanol and carbon monoxide (Fig. 3). The increase in the temperature above the temperature of complete consumption of oxygen leads to a partial decay of methanol. In our experiments such a decay was fast due to relatively low pressure and high temperature, and apparently occurs at the interaction

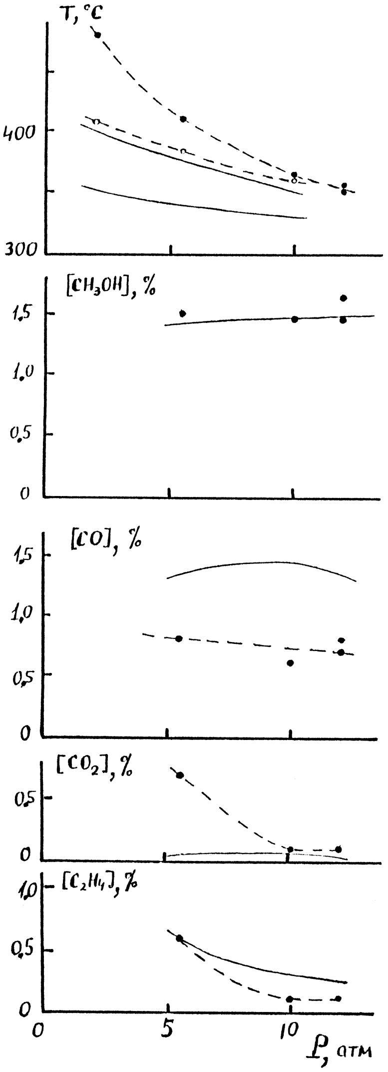

Fig. 4. Effect of pressure on temperature at the beginning of reaction (1) and temperature of complete conversion of oxygen (2), and on formation of products (vol% in gas flow). $[C_2H_6]_0=30\%$; $[O_2]_0=2.8–3.7\%$; $t_{res}=25$ s. Points and dotted lines – experimental data; solid lines – results of simulation.

of methanol with the surface. The model does not take into account such processes. We suppose that the oxidation of carbon monoxide into carbon dioxide occurs simultaneously accompanied by a sufficient change in their concentrations as is shown in Fig. 4. To our regret, this kinetic model does not provide the adequate description of this process. However, all previous models do not give an acceptable description of the carbon dioxide yield [3]. It indicates our poor understanding of the kinetics of its formation at low temperature methane oxidation. The experimental yield of ethylene remains practically unchanged if the temperature of complete oxygen conversion is achieved, although the theoretical curve shows it to rise (Fig. 3).

Even the limited pressure range of this work shows well enough the strong dependence of the temperature on the process and methanol yield from pressure (Fig. 4). However, when the pressure is increased above 10 atm the yield of undesirable products – carbon oxides and ethylene – drops. However, this limited pressure range does not give the real picture of the dependence of alcohols yield on pressure.

We have very limited experimental data on the oxidation of methane–ethane mixtures at higher pressures: a set of our experiments on pilot installation [7] at ethane concentration from 0% to 22% and $P=100$ atm (Fig. 5) and results of previous studies [8,9]. Our data for $P=100$ atm which is not optimal for oxidation of mixtures with a high content of ethane show the increase in the yield of alcohols (by approximately 1.5 times) with the increase in the concentration of ethane from 0% to $\approx$6% (Fig. 5). But then this yield drops again. Thus, as in the low pressure case, both theory and experiment show the extreme dependence of methanol yield from ethane concentration. The theoretical simulation gives some higher values of methanol and formaldehyde yields at $P=100$ atm, especially at high ethane concentrations. As it was pointed out in [7], this discrepancy may partially be accounted by the incomplete gathering of liquid products. It is evident that the further correction of the model is still needed.

The experimental dependence of formaldehyde/methanol ratio shows deep minimum at $[C_2H_6]_0\approx 5\%$ [7] similar to results obtained in [9] for the same oxygen concentration and pressure of 40 atm. The ratio of ethanol/methanol in products monotonously increased with ethane concentration. The comparison of our data with that of the study of Lodeng et al. [9] leads to a conclusion that this ratio increases also with pressure [7]. It is in accordance with the known rise of this ratio with pressure at oxidation of pure ethane where at $P=90$ atm it gains the value 6 [8].

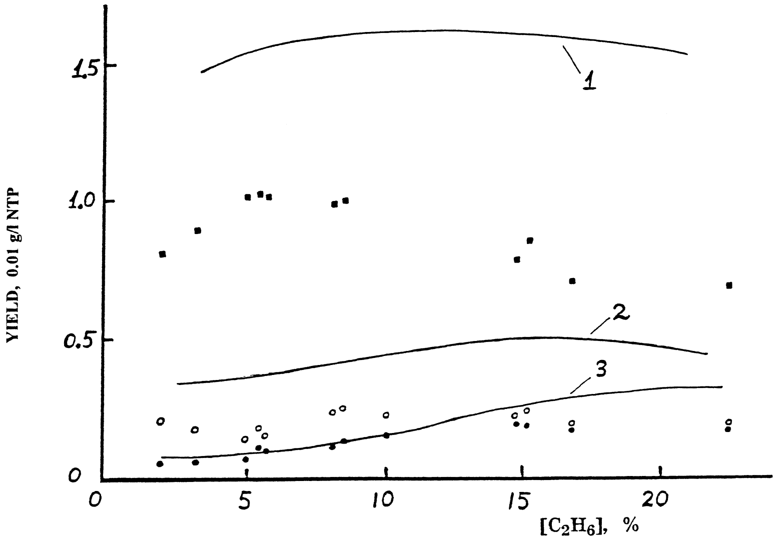

Fig. 5. Effect of ethane concentration on product yields (0.01 g/l NTP). $[O_2]_0$=2.7–3.0%, P=100 atm, T=350°C. (■) CH_3OH; (○) CH_2O; (●) C_2H_5OH. Points – experimental data; solid lines – results of simulation.

4. Conclusions

Despite the limited pressure range in the main part of this study the experimental results demonstrate noticeable increase in the total selectivity of formation of alcohols (methanol and ethanol) in the oxidation of methane–ethane mixtures in comparison with the oxidation of pure methane. This study also shows the possibility of obtaining high selectivity of alcohol formation at oxidation of such mixtures at relatively high oxygen concentrations (up to 7%). So, significantly higher conversion of hydrocarbons may be achieved. A rapid increase in the ethanol/methanol ratio with ethane concentration and pressure was observed.

It should be stressed that despite the satisfactory coincidence between the majority of calculated and experimental parameters, the experimental conditions of this work were not optimal for their comparison with the kinetic simulation of homogeneous gas phase process. The low surface/volume ratio due to the low diameter of the reactor, the relatively long residence time and relatively low pressures make possible a significant contribution of heterogeneous reactions on the surface of the reactor influencing the total kinetic of the process. The complete accounting of these heterogeneous reactions always involves great difficulties. So, the further improvement of the kinetic model must rely on experiments obtained in more homogeneous conditions.

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