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# Oxidative conversion of light alkanes diluted by nitrogen, helium or methane



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#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- Gas-phase oxidation of diluted C<sub>2</sub>-C<sub>5</sub> alkanes proceeds via chain-branching mechanism.
- Both hydrocarbon and oxygen convert almost similarly in space and time.
- Oxygen significantly increases the rate of the conversion and decreases its time.
- Oxygen inhibits the formation of heavy products.
- The nature of diluting gas significantly influences on the conversion.

#### ARTICLE INFO

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#### 1. Introduction

Recent development in unconventional gas production has multiplied its resources and decreased the price fivefold relative to that of petroleum [1]. Abundant resources and low prices make unconventional natural gas very attractive as petrochemical feedstock and increase the interest to its oxidative conversion to basic petrochemicals. But the oxidative conversion of light alkanes is much complex technological task than conversion of liquid hydrocarbons. It needs high temperatures and intensive heat fluxes. Because the most efficient way to introduce heat into hydrocarbon

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#### ABSTRACT

Abundant resources and low prices make natural gas very attractive as petrochemical feedstock and increase the interest to its oxidative conversion to basic petrochemicals. The paper presents results of gas-phase oxidative conversion of light  $C_2-C_5$  alkanes diluted by nitrogen, helium or methane  $([C_nH_{2n+2}]_0 \leq 5\%)$  at low oxygen  $[O_2]_0/[C_nH_{2n+2}]_0 = 0.2-1$ , atmospheric pressure and temperatures 500–750 °C. Even significantly diluted, light alkanes display a chain-branching behavior at oxidation with a sharp transition trough a self-ignition limit. Oxygen significantly increases conversion and decreases reaction time, especially at intermediate temperatures below that of thermal cracking. The nature of diluting gas significantly influences on the process.

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gas is the oxidation of small fraction of hydrocarbons to  $CO_2$  and water, it explains the rising interest to the partial oxidation of light  $C_2-C_5$  hydrocarbons that compose the principal admixture to methane in natural gas.

At high temperatures, which are necessary even for the catalytic activation of light alkanes, gas-phase processes play significant role and in some cases even predominate. It is not only makes very important thorough elucidation of the role of gas-phase reactions at catalytic conversion of light hydrocarbons but, as well, opens the possibility for homogeneous gas-phase processes which need no catalyst, thus significantly facilitates the conversion of complex mixtures of hydrocarbons with very different reactivity such as real natural gases. Especially it is important to elucidate the role of oxygen because it not only increases the rate of reaction and





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decreases its temperature, but, as well, inhibits the formation of heavy products including soot and decreases the selectivity to such important products as olefins.

Temperature is the main parameter that governs the oxidation of light alkanes and determines the formation of principal products at their partial oxidation. But temperature limits of formation of such principal products as oxygenates, olefins and syngas. at partial oxidation of methane and its heavier homologues significantly differ [2,3] which makes it possible selectively oxidize  $C_{3+}$  alkanes just in the natural gas without conversion of methane itself [4,5].

The aim of this study is the investigation of the kinetics of gas-phase oxidation of light  $C_2-C_5$  alkanes diluted by inert gas or methane  $([C_nH_{2n+2}]_0 \leq 5\%)$  at low oxygen  $[O_2]_0/[C_nH_{2n+2}]_0 = 0.2-1$ , atmospheric pressure and in the temperature range 500–750 °C. We believe that this investigation will provide valuable material for more detailed understanding of the mechanism of the oxidation of light alkanes in a wide range of conditions interesting for the practical realization.

#### 2. Experimental part

Experiments were conducted at atmospheric pressure in a flow quartz reactor with i.d. 14 mm and the length of isothermal zone 200 mm. Three independent electrical heaters with automatic regulation of temperature by separate thermocouples inside the rector provide almost uniform temperature profile. Taking into account the surface of quartz pockets for thermocouples, the surface to volume ratio S/V was 5.4 mm<sup>-1</sup>. To elucidate the influence of the inner surface of the reactor, in some experiments the second reactor with i.d. 8 mm and S/V ratio 13.3 mm<sup>-1</sup> was used. In several experiments a thin (~4 mm) layer of the industrial catalyst IPM-0.2 for isomerization of pentane–hexane fraction with 0.2 Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (fraction 0.5–0.8 mm) was placed at the entrance of the reactor. The contact time with catalyst (~0.06 s) was at least 20 times less than the complete reaction time.

Experiments were conducted in the temperature range 500–750 °C with the use of three diluting gases: nitrogen, helium or methane. Prepared in advance hydrocarbon–oxygen–buffer gas mixture was fed from cylinder trough the gas controller with a gas flow in a range from 2.4 to 25 ml/s which at 700 °C corresponds to the residence time from 0.35 to 3.6 s. The most of experiments were made at alkane concentration in buffer gas 5 mol.% with the mole ratio  $[O_2]_0/[C_nH_{2n+2}]_0$  from 0.2 to 1. But in some experiments aimed on the investigation of the influence of alkane concentration, it was varied from 2 to 9.2 mol.% at constant ratio  $[O_2]_0/[C_nH_{2n+2}]_0 = 0.5$ . Taking into account the low concentration of hydrocarbon, experimental conditions can be considered as almost isothermal, with experimental heating in the most cases below 5 °C.

Products were analyzed by GC equipped with several columns and detectors. Carbon was usually balanced within  $\pm 4\%$ . The concentration of water was calculated from the oxygen balance. More detailed description of experimental equipment and conditions is given elsewhere [6,7].

Experimental investigation of the oxidation of ethane was accompanied by the kinetic modeling with the use of the model for partial oxidation of  $C_1-C_2$  hydrocarbons, specially developed for the temperature range 600–1200 K and pressures from 1 to 100 atm, according to principles described in [8]. This model includes 454 elementary reactions [6] with all kinetic parameters taken from independent literature sources, predominantly NIST database [9]. These parameters were not varied or adjusted anymore during the course of calculations. All calculations were conducted for isothermal conditions with the use of the package Kintecus V450 [10].

#### 3. Results and discussion

The temperature of the noticeable radical-chain oxidative conversion of any particular hydrocarbon strongly depends on the composition of reaction mixture and reaction conditions. Due to numerous literature data [11], below 600 °C the noticeable oxidative conversion of ethane proceeds only in the presence of catalyst or on the surface of the reactor. Among the main products, except of ethylene, there are  $CO_2$  and  $H_2O$ . At that the rise of the conversion with temperature is slow enough. If there is a significant void volume, above 600–650 °C the fast increase of the gas-phase process is observed which is accompanied by the decrease of the selectivity to  $CO_2$  and  $H_2O$  and the increase of the selectivity to CO,  $H_2$  and  $CH_4$ .

The relative input of heterogeneous and homogeneous reactions depends on the properties of catalyst, its amount and the void volume of reactor, thus determining the composition of products [11]. At gas-phase oxidation the interaction of alkyl radicals with oxygen and oxygen containing radicals lead to the formation of oxygenates with their subsequent oxidation mainly to CO. In the presence of catalyst, on the contrary, the deep oxidation on its surface leads to significant yield of CO<sub>2</sub> and, as a result, low ratio CO/CO<sub>2</sub>. As a consequence, the catalytic oxidation (oxycracking, oxypyrolysis) of ethane on the active catalysts usually reveals the strong quantitative and time difference in the conversion of oxygen and ethane. For example, in our experiments in the presence of a thin layer of Pt catalyst at the entrance of the reactor, it was observed almost complete conversion of oxygen (~95%) already at low temperatures beginning from 300 °C (Fig. 1). Complete conversion of oxygen was accompanied by very low conversion of ethane  $(\sim 10\%)$  corresponding to its stoichiometric deep oxidation to CO<sub>2</sub> and H<sub>2</sub>O, the only detectable products at these conditions. Because oxygen practically completely consumes in the thin layer of the catalyst, further conversion proceeds at oxygen-free conditions. So the further increase of the conversion of ethane was observed only at temperatures above 650 °C (Fig. 1b) which corresponds to its thermal gas-phase cracking with increasing the selectivity to ethylene.

Very different behavior was observed in a void reactor. The conversion of both reagents begins only at temperatures above 600 °C and proceeds very similarly (Fig. 1). In this case oxygen presents in the significant part of the reactor thus providing real oxidative conditions. Very similar observations were made in [12], where complete conversion of oxygen at the oxidative dehydrogenation of ethane in the presence of mixed alkaline-earth and rare-earth oxides was attained already at 600 °C. This conversion of oxygen was accompanied by relatively low conversion of ethane. But in the absence of catalyst even at 750 °C the conversion of oxygen was only 80% with that of ethane 60%, thus both reagents were converted very similarly.

Although quartz surface of reactor walls cannot be considered as absolutely inert, experiments in reactors with different diameters (different surface to volume ratio S/V) have shown very similar results. The only difference in the reactor with smaller diameter and thus of about 2.5 times higher ratio S/V was the temperature shift of about 50 °C to a higher temperatures for attaining the same conversions, which can be interpreted as the retarding effect of the surface, presumably, due to the surface termination of radicals.

The similarity in the conversion of both reagents that was observed at high temperatures up to the temperature of complete oxygen conversion (Fig. 2) is one of the main features of the gasphase oxidation of light alkanes. At higher temperatures the rate of the increase of the conversion of ethane with the increase of temperature significantly drops. This further increase is presumably the sequence of the increasing input of the thermal cracking and thermal dehydrogenation of ethane. As it follows from Fig. 2, Download English Version:

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