

Brief Communications

Kinetic limit of the ethane and ethylene yield in the gas phase condensation of methane

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A kinetic simulation of the initiated oxidative condensation of methane in the gas phase showed that the additional generation of methyl radicals *via* the reaction $\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HO}_2$ causes a nearly tenfold increase in the C_2 hydrocarbon yield. However, a kinetic limit of the yield exists that is close to that determined in experiments on the catalytic oxidative condensation of methane.

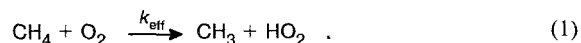
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Oxidative condensation of methane (OCM) into ethane and ethylene is one of the most promising ways of converting natural gas into more valuable chemicals. In most investigations, the process is carried out at atmospheric pressure and 900–1200 K using catalysts.^{1,2} A non-catalytic process also yields ethane and ethylene under similar conditions, although with less efficiency. According to the common mechanism of catalytic OCM, the interaction of oxygen with a catalyst surface results in dissociation of methane molecules into hydrogen and methyl radicals at the catalyst active centers. The methyl radicals are then desorbed into the gas phase, where C_2 hydrocarbons are formed.^{1,2} This OCM mechanism can be compared with that of gas-phase OCM, with the addition of a new source of methyl radicals.

We performed a kinetic simulation of the influence of the additional generation of methyl radicals on gas-phase OCM under conditions similar to those for the catalytic experiments. We used a reliable model of meth-

ane oxidation^{3,4} to which we added a series of elementary reactions, that are significant at higher temperatures (900–1200 K). This approach has been tested previously in a simulation of the experimental results^{5,8} of gas-phase OCM. The above works cover a wide range of temperatures (730–1100 K), pressures (1–62 atm), and methane-oxygen ratios (5–10) under isothermal and nonisothermal conditions. Satisfactory agreement between the experimental results and those of the model was obtained in all cases for such basic parameters as the yield and distribution of the main products and the characteristic time of the reaction. It should be stressed that we deliberately did not change any of the kinetic parameters of the model except the dependence of some rate constants on pressure.

The reaction (1) with an effective rate constant, k_{eff} , was chosen as the additional source of methyl radicals:



We simulated the changes in the rate of the production of methyl radicals by varying k_{eff} . Reaction (1) is known to occur under homogeneous and heterogeneous conditions.

The results of the simulation of gas phase OCM, with the additional radicals generated *via* reaction (1), under typical conditions for catalytic OCM are shown in Fig. 1 (curve 1).

The result of the simulation performed is the discovery of the existence of a kinetic limit for the yield of C_2 hydrocarbons as the rate of radical generation *via* reaction (1) increases monotonically.

Assuming that the main role of the catalyst is the generation of methyl radicals in the gas-phase reaction, it was of interest to study the initiation process (Eq.2).



In reaction (2) substance A is not consumed (see Fig. 1, curve 2). However, in this case, the formation of the methyl radicals does not involve oxygen, and an increase in the rate of reaction (2) becomes independent of the initiation reaction when the characteristic time of radical recombination is less than that of their reaction with oxygen. In addition, excluding the oxygen from the reaction scheme not only results in an increase in the yield of C_2 hydrocarbons, but also enhances the selectivity of C_2 hydrocarbon formation up to 100 %, because hydrocarbons become the only reaction products of the methyl radical in the absence of oxygen.

Reactions (3) and (4) were considered as an alternative possibility:



In this case, the formation of C_2 hydrocarbons is possible only after the reaction of the radicals produced with the initial reagents. This is more representative of the real process, and here too a kinetic limit of the yield of C_2 hydrocarbons is observed.

A comparison of the simulation results for gas phase OCM with those of the catalytic experiments shows that, in the absence of additional initiation, the yield of the C_2 hydrocarbons (about 2.5 %) is consistent with the results for less active catalysts (in particular, CaO). However, increasing the rate of radical generation allows one to reach a C_2 hydrocarbon yield comparable with those for the best catalysts (see Fig. 1, curve 1). Nevertheless, even at very high rates of radical generation, the yield of C_2 hydrocarbons does not exceed the limiting value (22 %), which is very close to that assumed earlier (25 %).⁹

The high yield of C_2 hydrocarbons in catalytic OCM can be achieved at much lower rates of efficient generation than those calculated for the homogeneous simulation, because the catalyst produces methyl radicals in a very thin near-surface layer, where the probability of

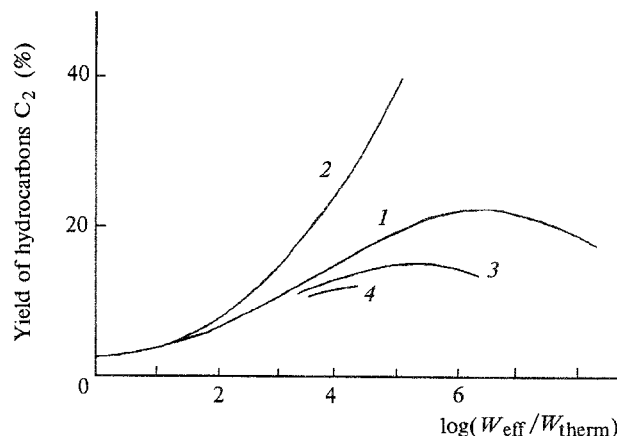


Fig. 1. Calculated yields of C_2 hydrocarbons at different ratios of the rates of the efficient homogeneous generation of radicals to the rates of thermal homogeneous generation, $W_{\text{eff}}/W_{\text{therm}}$. $T = 1073 \text{ K}$; $p = 1 \text{ atm}$; $\text{CH}_4 : \text{O}_2 : \text{N}_2 = 10 : 2 : 12.5$. The curve number corresponds to the number of the initiation reaction in the text.

their recombination into ethane is much more probable than the other possible reactions.

The simulation performed showed that the limit of the C_2 hydrocarbon yield in catalytic OCM seems to have a gas phase origination and, therefore, it can be determined from the results of the gas-phase simulation. A more accurate calculation of the limiting value should take into account the fact that the distribution of the methyl radicals within the gas volume is not homogeneous because they are generated on the catalyst surface. Exceeding the estimated kinetic limit of the yield can occur only in the case when the catalyst not only generates methyl radicals but also plays a decisive role in their subsequent transformations.

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