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THERMODYNAMICS AND KINETIC MODELING OF THE HOMOGENEOUS GAS PHASE REACTIONS OF THE OXIDATIVE COUPLING OF METHANE.

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SUMMARY
Thermodynamic calculations concerning methane activation have shown that in the equilibrium state hydrocarbons are only present in very small quantities. This is in contrast to experiments carried out under kinetically determined conditions, where considerable amounts of ethane and ethylene are formed via a radical mechanism. A computer model has been developed to simulate and analyze networks of those radical reactions operative in the oxidative coupling of methane.

INTRODUCTION
A new promising method for the production of ethylene is the partial oxidation of methane in the presence of a catalyst. To analyze the importance of radical reactions in this process, non-catalytic experiments were carried out in a micro flow reactor and simulated with a computer model. The model covers 164 elementary reactions, each described by an Arrhenius-like type kinetic equation. These equations are combined with an one dimensional reactor model, assuming plug flow and isothermal conditions in first instance. Axial temperature profiles are a built-in option.

RESULTS AND DISCUSSION
Thermodynamic calculations
The equilibrium composition of pure methane pyrolysis and that of pyrolysis in combination with methane oxidation have been calculated. The formation of elementary carbon was excluded, for reasons of simplicity. Figure 1 shows the conversion and yields (= the product of conversion and selectivity) of methane pyrolysis. The selectivities and yields have been defined on carbon bases. It is very clear that ethylene is the main hydrocarbon product at high temperatures in the chemical equilibrium state. However, the methane conversion is limited. If methane pyrolysis is carried out at elevated pressure, see Figure 2, the conversion is even lower. When the pressure is decreased, the product composition shifts from alkanes to alkenes to alkynes, C3's being the main products, when the pressure is decreased. C3 hydrocarbons are only present in small amounts.
When oxygen is added, the methane conversion is much higher, due to the high Gibbs free reaction energy of oxygen with hydrocarbons. In the equilibrium state the oxygen conversion is always complete when hydrocarbons are in excess. A cumulative volume fraction diagram of equilibrium compositions (initial CH₄/O₂ = 10) is plotted in Figure 3. At
moderate temperatures the methane is converted into hydrogen and carbon monoxide. At
higher temperatures, however, the products include CO₂, water and hydrocarbons, with poor
yields of the latter.

Gas phase experiments at varying residence time, Figure 4, show that kinetics govern the
product distribution. The experiments were carried out in a quartz reactor of a micro flow
reactor set-up, described elsewhere (ref. 1). Short contact times give high selectivities with
respect to the desired C₃H₈ and C₄H₁₀, but at poor conversions, whereas long residence times
(left part of the figure) favours the formation of carbon oxides and high conversions. The
oxidation of CO to CO₂ in the gas phase (ref. 2) is rather slow, which explains the very long
residence times required to get carbon dioxide. Note that the points on the vertical axis,
representing the calculated chemical equilibrium state, are covered very nicely by
extrapolations of the experimental values. In agreement with the assumption that the
formation of elementary carbon was negligible and could be omitted in the calculations, no
carbon deposits were detected as long as oxygen was present in the outlet stream of the
reactor.

Model

As is shown in Figure 4, oxidative coupling of methane can occur in the homogeneous gas
phase. A computer program has been developed to simulate and analyze those reactions. The
program is based on a combination of a reaction and a reactor model. The latter is modelled
as an one dimensional ideal plug flow reactor. The gas phase reactions take place according
to a complex free radical mechanism which can be described by a set of elementary
reactions, see Table 1. Each of these reactions is characterized by an extended Arrhenius
expression for the reaction rate constant: \( k = A \cdot T^b \cdot \exp \left(-\frac{E_{\text{act}}}{RT}\right) \)

In which
- \( A \) = frequency factor
- \( b \) = non-linearity coefficient [-]
- \( T \) = absolute temperature [K]
- \( E_{\text{act}} \) = energy of activation [kJ/mol]
- \( R \) = gas constant [kJ/(molK)]
- \( A T^b \) for a first order reaction [s⁻¹]
- for a second order reaction [m³/(mol²s)]
- for a third order reaction [m³/(mol³s)]

An important feature of the model developed is its option for a kinetic sensitivity analysis.
It determines the influence of each elementary reaction on the product distribution. The
principle of the method is that the frequency factor of each reaction in turn is divided by a
constant, for example 10, and that new concentrations resulting from the calculations are
used to compute integral sensitivity factors. These are defined as \( s_i = \Delta \ln c_i / \Delta \ln k_i \), in which
Table 1
Set of elementary radical reactions as used in the model. (Units, see text) (Ref. 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14)
Note that the ethylene selectivity predicted by the model is too low. This requires further attention. The negative ethylene selectivities at low methane conversion are caused
Comparison of experimental data (symbols) with simulations (lines).

Figure 5 Comparison of experiments (symbols) with simulations (lines).
Conditions: CH₄/O₂ = 10, CH₄/He = 0.8, P = 1 bar.

Figure 6 The simplified gas phase reaction scheme with the main reaction paths. The width of an arrow indicates the importance of that reaction path.
Conditions: T = 800°C, P = 1 bar, CH₄/O₂ = 5.

by (calculated) conversion of traces of ethylene present in the feed.

Another powerful tool of the model is the integration of individual reaction rates over the reactor, thus demonstrating the most important reaction pathways. It appears that H, OH, HO₂, and CH₃ are the most reactive species. After an induction period in which the radical concentrations are built up, they stay fairly constant at typical concentrations of 10⁷ - 10⁴ mol/m³. Figure 6 shows the main reactants and reaction pathways of carbon containing compounds. The thickness of the arrows corresponds to the contribution of the respective reaction. It may be obvious that the C₂-oxygenates, CH₂, CH, CH₂OH and other omitted species are unimportant. The most important initiation reaction no. 2, in which oxygen reacts with methane, appears to contribute very little to the methane conversion, and the same applies to other initiation reactions. The formation of CH₃ radicals from methane appears in the scheme as a rapid system of equilibrium reactions in which various radicals are involved. In agreement with experimental results, the quantities of C₂-products are very limited, not because they are oxidised very fast, but because of their low rate of formation, see Figure 6. The C₂-species prefer to undergo hydrogen abstraction rather than coupling with methyl radicals. Ethane and ethyl radicals are hardly oxidised and the formation of CH₃ from C₂H₆ is negligibly small, which implies that extremely high initial ethylene selectivity of ethane oxidation should be achievable. This is confirmed, although not shown here, experimentally.
The trends of the effects of temperature, dilution and \( \text{CH}_4/\text{O}_2 \) on the selectivity of the reaction are very similar for both homogeneous gas phase reactions and the Li/MgO catalyzed reactions. We therefore assume that the reaction scheme is valuable for the catalytic reactions as well. A major difference is the formation of \( \text{CH}_3 \) radicals, the key component for a good \( \text{C}_2^+ \) selectivity, see Figure 6. A catalyst favours the (irreversible) formation of this radical (ref 3.), involving oxygen and resulting in much higher levels of \( \text{CH}_4 \) radicals. Thus higher rates and higher coupling efficiencies may be achieved using a catalyst. In Table 2 simulations and experiments are shown, for both catalyzed and homogeneous gas phase reactions. The catalyst is simulated by a set of reactions that equals the overall reaction: \( 4 \text{CH}_4 + \text{O}_2 \rightarrow 4 \text{CH}_3 + 2 \text{H}_2\text{O} \). As is shown, indeed the higher \( \text{CH}_3 \) radical formation rate results in a higher reaction rate and a higher ethane selectivity. The decrease in reaction time is however too large compared to the experimental value. Therefore, it is assumed that the catalyst also acts as a radical sink. Radicals collide with the surface and react to less active molecules. This lowers the radical concentrations and slows down the conversions of methane and oxygen.

**CONCLUSIONS**

In the calculated chemical equilibrium state, ethylene is the main product of methane pyrolysis when the formation of elementary carbon is excluded. The ethylene yield however is limited, due to a limited methane conversion that even gets worse when the pressure is increased. Addition of oxygen leads to a much higher methane conversion, however at low \( \text{C}_2^+ \) selectivities. Extrapolation of the results of gas phase experiments to the condition of infinite residence time gives an excellent fit with values calculated for the equilibrium state.

The model developed simulates the experiments correctly. The main carbon reaction path goes via \( \text{CH}_n, \text{C}_2\text{H}_n, \text{C}_3\text{H}_n \) towards \( \text{C}_n\text{H}_n \) that is oxidised rapidly into CO. The most active reaction species in the homogeneous gas phase are the radicals \( \text{H}, \text{OH}, \text{CH}_3 \) and \( \text{OH}_2 \). \( \text{C}_2^+ \)-hydrocarbons are hardly produced due to their low rate of formation. Simulations have made clear that the Li/MgO catalyst cannot be described as a methyl radical producer only: probably it also acts as an (aselective) radical consumer.
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