investigating the x-ray photoelectron spectra of the zeolites themselves, it has been shown that it is the cationic form of the metal which is catalytically active in ethylene oligomerization. Metallic Pd is inactive in these catalysts under the conditions of the present work.

LITERATURE CITED


THE TEMPERATURE DEPENDENCE OF THE RATES OF BRANCHING-CHAIN PROCESSES

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Study of the kinetics of branching-chain processes (BCP) usually starts from the assumption that the reactions under consideration are carried out under isothermal conditions [1-3]. Thus it was assumed in [2] that the temperature variation of the rate of the branching-chain process is covered by an Arrhenius equation, while the rate of the limiting step in the ignition of hydrogen, a model BCP, was assumed to be a linear function of the temperature in order to simplify the calculations of [4]. The equations for the temperature variation of the reaction rate given in [1, 2] apply only to the so-called stationary isothermal chain reaction, which is to say to an isothermal process in which the chain branching rate is less than the rate of chain breaking. The role played by nonisothermal BCP's in the combustion of H₂ has been considered in [5, 6] where an electronic computer was used to solve the system of kinetic and heat balance equations applying to the reacting mixture. The temperature variation of the reaction rate was not discussed in either of these last two papers.

It can be shown theoretically [7] that one type of temperature dependence applies to reaction rates in BCP systems in which branching predominates over breaking (nonstationary reactions) and still another type applies to rates in systems in which chain breaking is the predominant process. The expression for the reaction rate of the nonstationary process at low degree of advancement contains an exponential Boltzmann factor with positive sign.

The present work was an experimental study of the temperature dependence of the rate of combustion of stoichiometric H₂-O₂ mixtures, reactions in this system being considered as model BCP's. Reactions were carried out at pressures near the first ignition limit, where the reaction mechanism was sufficiently simple to permit the attainment of definitive experimental data. An additional consideration in deciding to work in this region was the fact that heterogeneous chain breaking here transfers a large portion of the system energy to the reactor walls [8], thereby assuring that self-heating remain within reasonable limits. Since
the combustion process extends over relatively long periods of time, the reaction kinetics could be followed rather closely by simultaneous measurement of the various parameters of the reacting system.

It is generally agreed that the following reaction scheme applies to the early stages of the combustion process where second-power chain breaking has not yet become a factor of importance

\[
\begin{align*}
    H_2 + O_2 & \rightarrow 2OH \\
    OH + H_2 & \rightarrow H_2O + H \\
    H + O_2 & \rightarrow OH + O \\
    O + H_2 & \rightarrow OH + H \\
    H + \text{wall} & \rightarrow \text{chain breaking}
\end{align*}
\]

(0) \hspace{1cm} (I) \hspace{1cm} (II) \hspace{1cm} (III) \hspace{1cm} (IV)

The rate of consumption of O\(_2\) is given by the equation

\[
W = k_a [O_2][H] + \frac{\omega_0}{2}
\]

in which \(k_a\) is the rate constant for step (II) in the above scheme, \(\omega_0\) is the rate of spontaneous chain initiation, and \([O_2]\) and \([H]\) are the respective concentrations of \(O_2\) and \(H_2\).

Once the induction period has been passed through, combustion proceeds largely through combination of the system components with the active centers [1, 9]. Under these conditions \(\omega_0/2 \ll k_2 [O_2][H]\). The method of stationary concentrations can be applied in the initial stages of the reaction where the active-center concentration is still relatively low, no account being taken of the effect of second-power chain breaking at this point [10]. This leads to the following expression for the time rate of change of the H atom concentration:

\[
\frac{d[H]}{dt} = \varphi[H]
\]

(2)

Here

\[
\varphi = 2k_2 [O_2] - k_4
\]

(3)

\(k_4\) being the rate constant for the i-th step in the above reaction scheme. Integration of (2) with subsequent substitution back into (1) gives

\[
W = k_a [O_2][H] \int_0^t \varphi dt
\]

(4)

\([H]\)\(_0\) being the concentration of hydrogen at \(t_0\), the point at which \(\omega_0 \ll \varphi \cdot [H]\) for the first time. Estimation of \(t_0\) was based on an application of the equation [1, 9]

\[
[H] = \frac{\omega_0}{\varphi} (e^{\varphi t} - 1)
\]

(5)

to the isothermal reaction occurring during the process induction period. It is seen from this equation that \([H] \gg \omega_0\) when \(t_0 > 3/\varphi\). Since \(k_a\) is an exponential function of the temperature, it follows from Eqs. (3) and (4) that the effect of temperature on the reaction rate at \(\varphi > 0\) must be much more pronounced than that predicted by the Arrhenius law. In fact, the effect of temperature change becomes more pronounced as the frequency of chain branching rises and the value of \(\varphi\) increases.

Second-power chain breaking through the reaction