Brief Communications

Concerning the dependence of the selectivity of the formation of ethane and ethylene on the degree of methane conversion during its oxidative coupling

V. I. Vedeneev, V. S. Arutyunov, and V. Ya. Basevich*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Science,
4 ul. Kosygina 117334 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

The dependences of the maximum selectivity and the limiting yield of C_2 hydrocarbons on the degree of methane conversion during its gas-phase oxidative coupling were calculated by means of kinetic simulation. The correlation between the results of the calculations and the rersults obtained in the experimental studies dealing with catalytic oxidative coupling of methane is discussed.

Key words: oxidative coupling of methane, kinetic simulation.

The dependence of the selectivity of the formation of C_2 hydrocarbons (ethane and ethylene) on the degree of conversion during the oxidative coupling of methane (OCM) is an important criterion for determining the maximum achievable yields of these products and the practical perspectives of the process. The fact that the selectivity of the formation of C_2 hydrocarbons decreases as the degree of methane conversion increases in both gas-phase and catalytic OCM is of no doubt. Based on the analysis of the experimental data published, it has been suggested that a limiting value for the yield of C_2 hydrocarbons in this process, which is equal to ~25 %, exists.[1] However, more recently, higher yields, of up to 32 %, have also been reported.[2] It has been suggested many times that the limit observed has a kinetic nature.

The yield of C_2 hydrocarbons in gas-phase OCM is low and does not exceed several percent. The most generally accepted mechanism for catalytic OCM, in which considerably higher yields are achieved, involves the catalytic activation of methane on the surface and the ejection of methyl radicals into the gas phase, where all of the subsequent transformations occur.[2]

We analyzed the mechanism of gas-phase OCM under the conditions of the additional generation of methyl radicals.[3] The analysis was carried out for the experimental conditions[4] $P = 0.1$ MPa, $T = 1073$ K, $CH_4/O_2 = 5$. It was found that when the rate of the generation of methyl radicals increases, the yield of C_2 hydrocarbons only increases to a definite limit, which virtually coincides with the limit of the yield of C_2 hydrocarbons in the catalytic experiments.

The purpose of the present work has been an analysis of the dependence of the selectivity of the formation of C_2 hydrocarbons in initiated OCM on the degree of methane conversion. The dependence obtained is shown in the known plot in Fig. 1 (curve *1*). It can be seen that

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 568—570, March, 1995.

1066-5285/95/4403-0551 $12.50

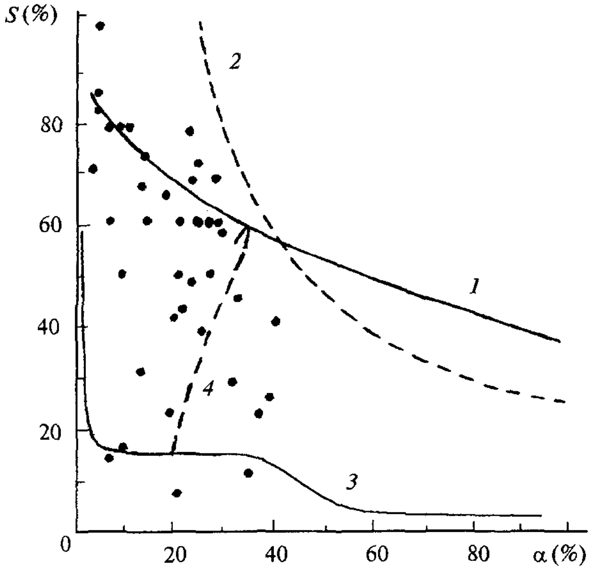

Fig. 1. The dependence of the selectivity of the formation of C_2 hydrocarbons (S) on the degree of methane conversion (α) (T = 1073 K, P = 1 atm): The kinetic calculation for initiated gas-phase OCM (*1*); the limit of the 25% yield of C_2 hydrocarbons (*2*); the kinetic calculation for non-initiated gas-phase OCM (*3*); the calculation of the dependences of the degree of methane conversion and the selectivity of the formation of C_2 hydrocarbons during the variation of the effective rate of the generation of methyl radicals in a $CH_4 : O_2 : N_2 = 10 : 2 : 12.5$ mixture (*4*). The dots correspond to the experimental results obtained for catalytic OCM.[1]

this dependence differs from the hypothetical hyperbolic dependence suggested in Ref. 1 (Fig. 1, curve *2*). The calculated yield of C_2 hydrocarbons increases as the degree of methane conversion increases and reaches ~36 % at high degrees of conversion (Fig. 2, curve *a*).

When comparing the results of the calculations carried out for the gas-phase process with those reported for the catalytic process, one should take into account that in the simulation we assumed that the additional generation of methyl radicals occurred uniformly throughout the reactor bulk. The catalytic generation of methyl radicals on the surface and the subsequent diffusion of the reactants under the conditions of quick recombination of the radicals may lead to somewhat different values of the yields.

The presence of the kinetic limit of the gas-phase formation of C_2 hydrocarbons actually sets the same limit for catalytic OCM, if one assumes that the catalyst only participates in the generation of the methyl radicals and has no effect on the subsequent processes that influence the formation of C_2 hydrocarbons. A juxtaposition of the dependence obtained with the results of kinetic studies shows that the overwhelming majority of the results lie below curve *1* or near it (Fig. 1).

Figure 1 (curve *3*) and Figure 2 (curve *b*) also show the dependences of the selectivity and yield of C_2 hydrocarbons on the degree of methane conversion calculated for the non-initiated reaction. It is noteworthy that the experimental results obtained with the least active catalysts (CaO, MgO) lie near the curve calculated for the non-initiated reaction. At the same time, the yield obtained experimentally for Sm_2O_3, which is one of the most active catalysts in this process, falls on the plot of the yield *vs.* the degree of conversion calculated for the initiated process (Fig. 2). All of the experimental results were taken from Ref. 1.

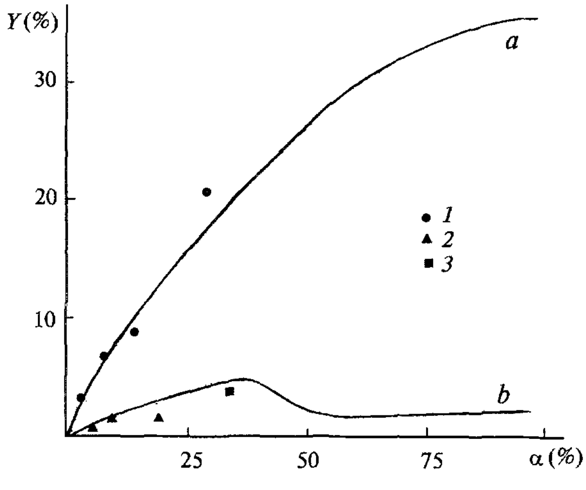

Fig. 2. The dependence of the yield of C_2 hydrocarbons (Y) on the degree of methane conversion (α) (T = 1073 K, P = 1 atm): The kinetic calculation for initiated gas-phase OCM (*a*); the kinetic calculation for non-initiated gas-phase OCM (*b*). The dots correspond to the experimental data taken from Ref. 1: Sm_2O_3 (*1*); CaO (*2*); MgO (*3*).

The kinetic model used in the calculations and the results of the simulation for a number of experimental works on gas-phase OCM have been published previously.[5,6]

References

1. J. G. McCarty, A. B. McEwen, and M. A. Quinlan, in *New Developments in Selective Oxidation*, Eds: G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990.
2. O. V. Krylov, *Catal. Today*, 1993, **18**, 209.
3. V. I. Vedeneev, V. S. Arutyunov, and V. Ya. Basevich, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 380 [*Russ. Chem. Bull.*, 1995, **44**, 372 (Engl. Transl.)].
4. J. W. M. H. Geerts, Q. Chen, J. M. N. van Kasteren, and K. van der Wiele, *Catal. Today*, 1990, **6**, 519.
5. V. I. Vedeneev, O. V. Krylov, V. S. Arutyunov, V. Ya. Basevich, M. Ya. Goldenberg, and M. A. Teitel'boim, in *New Developments in Selective Oxidation* 2, Eds. V. C. Corberan and S. V. Bellon, Elsevier, Amsterdam, 1990.
6. V. I. Vedeneev, O. V. Krylov, V. S. Arutyunov, V. Ya. Basevich, M. Ya. Goldenberg, and M. A. Teitel'boim, *Appl. Catal.*, 1995 (in press).

Received July 13, 1994