ELSEVIER

Catalysis Today 32 (1996) 157–162

CATALYSIS TODAY

Oxidation of methane in a wide range of pressures and effect of inert gases

Mikhail Yu. Sinev *, Yurii P. Tulenin, Olga V. Kalashnikova, Viktor Yu. Bychkov, Vladimir N. Korchak

Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin str., Moscow 117334, Russia

Abstract

The analysis of methane oxidation in a wide range of pressures (0.05–10 atm) demonstrates that the efficiency of CH_3 radicals recombination is of great importance for high selectivity of C_2 hydrocarbons formation. The relative efficiency of different "colliders" assisting the stabilization of exited $C_2H_6^*$ molecules increases in the series: *solid surface* > *Ar* > *He*. The increase of the overall reaction rate upon increasing pressure of the inert gases in the case of catalysts having a higher surface area and more developed pore structure is likely due to the contribution of the surface-induced chain reaction in the volume of pores.

Keywords: Methane oxidation; C_2 hydrocarbon formation; Pressure effect; Inert gases

1. Introduction

Catalytic oxidative coupling of methane (OCM) to C_2-hydrocarbons is well-known as a typical example of a heterogeneous–homogeneous reaction [1–3], i.e., the substantial stages of this process are located both on the surface of the catalyst and in the gas phase. In consequence, the reaction rate and the selectivity with respect to formation of different products are dependant both on the properties of the catalyst and on the conditions in the gas phase. Since pioneering works of Fang and Yeh [4], Keller and Bhasin [5], and Baerns et al. [6] a number of studies have been carried out to improve the activity and selectivity of oxide catalysts with respect to OCM products formation.

Attempts to optimize the conditions in the gas phase are not so numerous. In Ref. [7] the influence of the total pressure of the reactants on homogeneous OCM process has been studied. In this case the increase of methane conversion is caused by acceleration of the bimolecular initiation of the chain reaction. This conclusion was confirmed by kinetic simulation [8].

The influence of pressure on catalytic methane oxidation is much more complex likely due to overlapping of different effects. If the total pressure is increased at constant methane-to-oxygen ratio in reaction mixture, the rise of oxygen pressure should lead to a decrease of OCM selectivity (according to kinetic analysis carried out in Ref. [9]) due to increasing fraction

---

* Corresponding author.

PII S0920-5861(96)00175-7

of CH_3 radicals transformed into CH_3O_2 via the equilibrium reaction

$$CH_3 + O_2 \rightleftharpoons CH_3O_2. \tag{1}$$

On the other hand, since the formation of C_2-hydrocarbons proceeds via intermediate exited ethane molecule $C_2H_6^*$ in recombination of CH_3 radicals and its further stabilization in collisions with other molecules M

$$CH_3 + CH_3 \rightarrow C_2H_6^*(+M) \rightarrow C_2H_6, \tag{2}$$

the increasing total pressure should lead to an increase of selectivity due to three-body character of recombination process.

In the present work the oxidation of methane has been studied in a wide range of pressures at constant CH_4:O_2 ratio. To separate the effects of different factors, the total pressure has been varied by changing the pressures of the reactants and by addition of inert gases (He,Ar) to the mixture of methane and oxygen at their constant pressures. Both non-catalytic and catalytic processes have been studied. In the latter case, two catalysts of similar chemical composition, but of different morphologies have been used.

2. Experimental

The details of experimental procedure and reaction system for the measurements at elevated pressure (up to 30 atm) have been described elsewhere [10,11]. The same setup was used in our experiments at reduced pressures.

Two mixed neodymia–magnesia catalysts were used: 1% Nd supported on fused MgO (Cat. 1, specific surface area < 0.5 m^2/g) and 10% Nd on MgO obtained by decomposition of $Mg(OH)_2$ (Cat. 2, specific surface area 15 m^2/g).

Initial mixtures containing methane and oxygen in 9:1 ratio were used. Helium and argon were used as inert diluents. The experiments at elevated pressures were performed at constant pressure of $(CH_4 + O_2)$ mixture to which the inert gases at different pressures were added. The flow rates of the mixture were chosen to keep the reactants (methane and oxygen) flows also constant.

The experiments at reduced total pressures were performed without dilution of reactants at the flow rates decreasing proportionally to the pressure to keep the residence time constant.

3. Results

3.1. Elevated pressures

Three series of experiments were carried out at atmospheric and elevated pressures: without any catalyst, with Cat. 1, and with Cat. 2.

Compression of the reaction mixture by addition of inert gases at constant methane and oxygen pressures results in a complex variation of the rate of non-catalytic oxidation: depending on the type of inert gas, the temperature, and the range of pressures the rate of methane conversion (W) increases, decreases, and passes through the maximum or minimum. As a rule, these variations at 5–10 atm do not exceed 40% of initial rate at 1 atm, and in the same range of pressures at 700–900°C the rate of reaction in Ar is 1.3–1.5 times higher as compared to He (see Fig. 1). Simultaneously the addition of inert gas leads to the sharp acceleration of OCM products formation (see Fig. 1). Under the same conditions selectivity to C_2-hydrocarbons (SC_2) is substantially higher when argon is used as diluent.

If the reactor is filled with Cat. 1, both the reaction rate and SC_2 are significantly higher. In this case the shapes of W versus P and SC_2 versus P curves are similar to those in the empty reactor, but the effect of inert gas addition is much weaker (see Fig. 2). At 1–10 atm helium has almost no effect on the reaction rate and selectivity. The addition of argon leads to the slight increase of W and SC_2.

Cat. 2 is much more active and selective as compared to Cat. 1. That is why the series of

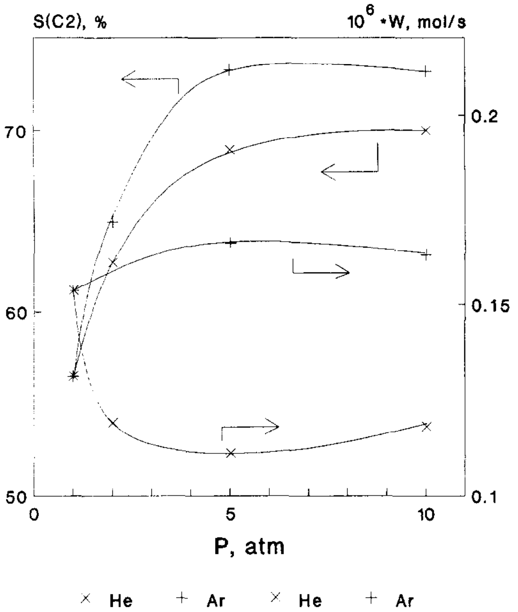

Fig. 1. C_2-selectivity and rate of methane conversion as the functions of total pressure; $P(CH_4)+P(O_2)=1$ atm; 800°C; no catalyst.

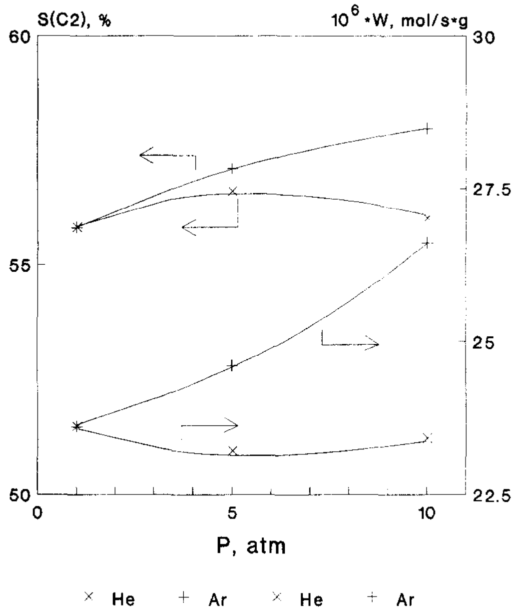

Fig. 2. C_2-selectivity and rate of methane conversion as the functions of total pressure over Cat. 1; 750°C; $P(CH_4)+P(O_2)=1$ atm.

experiments with this sample was carried out at much lower temperatures and we had to dilute the reactants with inert gases even when reaction was conducted at atmospheric pressure. However, the effect of inert gases on parameters of reaction over Cat. 2 is pronounced much stronger as compared to Cat. 1 (see Table 1). The lower the reaction temperature, the more

Table 1

Reaction rate (W), C_2-selectivity (SC_2) and H_2 concentration over Cat. 2 at different inert gas pressures; $m_{cat}=14$ mg, $P(CH_4)+P(O_2)=0.2$ atm

P_{tot} (atm)	Flow rate (ml/min)	t °C	10^6 W (mol/s g) He	10^6 W (mol/s g) Ar	SC_2 (%) He	SC_2 (%) Ar	$[H_2]$ (vol.%) He	$[H_2]$ (vol.%) Ar
1	50	525	6.1	7.8	2.3	5.0	0.17	0.33
		540	8.7	12.8	6.3	9.0	0.25	0.51
		560	12.8	17.6	10.4	13.3	0.35	0.65
		580	17.4	26.1	14.2	21.0	0.46	0.81
		600	24.4	35.2	20.3	28.4	0.53	0.89
		625	40.6	48.2	34.1	33.7	0.66	0.85
2	100	510	5.4	6.3	0	6.7	0.07	0.11
		530	8.8	13.3	7.1	18.3	0.10	0.23
		550	12.8	17.5	10.1	21.3	0.16	0.29
		575	20.7	27.5	18.7	23.2	0.23	0.36
		600	31.8	39.6	26.8	30.8	0.26	0.45
		625	38.9	48.0	26.7	36.0	0.27	0.37
5	250	525	9.0	12.5	0	4.8	0.03	0.08
		550	12.4	19.7	7.7	6.9	0.05	0.13
		575	25.2	31.4	21.4	22.8	0.10	0.16
		600	32.4	41.9	26.1	25.3	0.11	0.17
		625	45.4	52.5	36.4	33.8	0.12	0.18

pronounced is the effect of the nature of inert gas on C_2-selectivity. In the case of argon the starting W and SC_2 at $P(\mathrm{Ar}) = 0.8$ atm are substantially higher as compared to those in the presence of He, but the relative effect of increasing the argon pressure under the same conditions is less pronounced. In consequence, whereas increasing $P(\mathrm{He})$ from 0.8 to 4.8 atm at temperatures > 550°C causes the progressive increase of W and SC_2, selectivity in the presence of argon passes through the maximum at increasing $P(\mathrm{Ar})$.

Besides C_2 hydrocarbons, carbon oxides and water, molecular hydrogen is also present in the reaction mixture. Its formation is very sensitive to the type of inert gas. For instance, when Cat. 2 was used, the H_2 concentration was 1.5–3 times higher in the case of argon. However, the yield of hydrogen does not change upon variations of inert gas pressure.

3.2. Reduced pressures

Fig. 3 demonstrates that decreasing the pressure of the reaction mixture from 1.0 to 0.05 atm leads to a proportional decrease of the total rate of methane conversion (W) over Cat. 1.

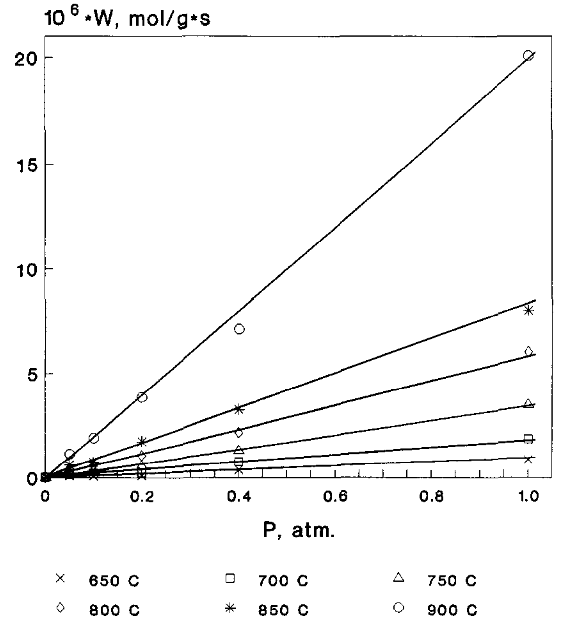

Fig. 3. Rate of methane conversion as the function of pressure of reactants over Cat. 1 (CH_4:O_2 = 9:1).

At relatively low methane conversions SC_2 increases upon increasing the total pressure and temperature. At higher conversion the consecutive total oxidation of C_2's becomes substantial. In consequence, the reversed trend was observed at temperatures > 800°C: SC_2 decreases upon increasing pressure at $P > 0.2$ atm.

4. Discussion

4.1. Non-catalytic oxidation

The influence of different factors on the selectivity of the heterogeneous–homogeneous OCM process may be discussed in terms of the kinetics of CH_3 radicals transformations. According to the analysis performed in Ref. [9] SC_2 cannot exceed the limit (S_{lim}) determined by kinetics and equilibrium of gas-phase reactions of CH_3 and CH_3O_2 radicals. As the first approximation

$$S_{\mathrm{lim}} = k_{\mathrm{app}} / \left[k_{\mathrm{app}} + K \cdot P(O_2) \cdot \Sigma \right], \qquad (3)$$

where k_{app} is the apparent 2nd-order rate constant of recombination reaction (2); K is the equilibrium constant of reaction (1); $P(O_2)$ is the oxygen pressure; and Σ is the sum of the effective rate constants of the bimolecular radical reactions of CH_3O_2 which lead to the formation of the total oxidation products.

On the other hand, since reaction (2) is a three-body process, k_{app} can be described in terms of a Lindemann-kind scheme of formation and transformations of excited ethane molecule during CH_3 radicals recombination [12] as follows:

$$k_{\mathrm{app}} = k_1 \cdot k_3 \cdot [M] / (k_2 + k_3 \cdot [M]), \qquad (4)$$

where k_1, k_2 and k_3 are rate constants of formation, decomposition, and relaxation of exited ethane molecule, respectively; $[M]$ is the concentration of molecules-"colliders" assisting the excited ethane molecule relaxation (in general: any molecule in the gas phase).

The shape of the SC_2 versus P curves (Fig. 1) is in a good agreement with Eq. (4), according to which the increasing total pressure must lead to the increase of recombination rate until it reaches the high-pressure limit ($k_{app} = k_1$). The difference in SC_2 at the same pressures in argon and helium baths indicates their different efficiencies as ''colliders''. As we mentioned above, this difference is much more pronounced at lower temperatures. This fact is in a good agreement with Eq. (3) and (4), if we assume that $k_3(Ar) > k_3(He)$.

The higher rate in the presence of Ar as compared to He is more difficult to explain. A special kinetic simulation is required to elucidate how the variations of recombination kinetics affect the rates of complex chain reaction.

4.2. Catalytic oxidation

Higher selectivity of methane oxidation in catalytic process may be due to the following factors: (i) higher rate of CH_3 radicals formation; (ii) high efficiency of the solid surface as a ''collider''.

In fact, C_2-hydrocarbons formation is a 2nd-order process with respect to CH_3 concentration. On the other hand, in addition to bimolecular processes taken into account in Ref. [9], oxidation products form via several reactions which are of the 1st order with respect to CH_3 and CH_3O_2 concentrations, such as

$$CH_3 + O_2 \rightarrow CH_2O + OH, \qquad (5)$$

$$CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3. \qquad (6)$$

In consequence, if the rate of CH_3 formation increases, their fraction undergoing recombination (and, consequently, SC_2) increases as well due to the higher kinetic order with respect to CH_3 concentration. The similar arguments were suggested in Ref. [13] to explain the effect of residence time on selectivity.

With respect to the efficiencies of different ''colliders'', since the number of channels of energy dissipation in solids is much higher as compared to inert gases, one may assume that the relaxation probability per collision in the former case is much higher. The frequency of collisions of excited ethane molecule with different particles in the gas phase and with the Cat. 1 surface are comparable. Due to this, helium has no effect, and argon has only a slight effect on selectivity.

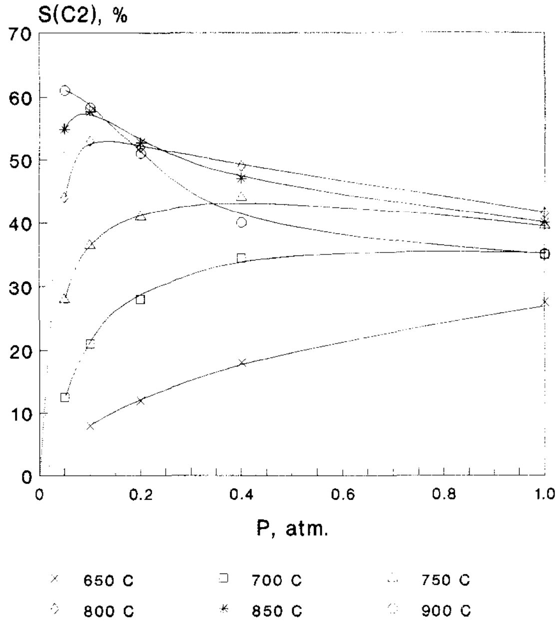

Fig. 4. C_2-selectivity as the function of pressure of reactants over Cat. 1 (CH_4:O_2 = 9:1).

In the experiments at $P < 1$ atm the joint influence of the rate of CH_3 formation and total pressure cause the increasing selectivity with total pressure (see Fig. 4), although according to Eq. (3) it should decrease at increasing $P(O_2)$, especially at lower temperatures.

The influence of inert gases sharply increases in the case of much more active Cat. 2 having more developed surface and pore structure (see Table 1). This effect may be explained as follows. The methane molecule interaction with surface active sites leads to the formation of CH_3 radicals. Their further transformation in the gas phase (i.e., in the space between the catalyst grains or in the volume of pores) may lead to the development of non-linear chain process due to branching reactions like

$$CH_3 + O_2 \rightarrow CH_3O + O, \qquad (7)$$

or H_2O_2 and CH_3OOH decomposition at lower temperatures.

In contrast with heterogeneous reactions, chain processes are known to develop non-linearly with time. The diffusional restrictions and, consequently, the residence time in pores of catalyst increased proportionally to the total pressure and to the square root of the average molecular weight of the gas mixture. This may lead to the additional conversion of reactants despite of constant formal residence time in the reactor. Since the molecular hydrogen formation likely occurs in the chain process, the high sensitivity of H_2 concentration to the type of inert gas may be considered as an indirect evidence for the contribution of homogeneous processes in methane oxidation over Cat. 2.

Comparison of the data given in Fig. 2 and in Table 1 shows that, because of more significant diffusion restrictions, this effect is much more pronounced in the case of inert gas of higher molecular weight (Ar) over the catalyst of higher surface area and more developed pore structure (Cat. 2). In consequence, the conversion of reactants is increased due to increasing contribution of surface-induced gas-phase reactions, causing a non-trivial effect of ''diffusion acceleration'' of overall process.

Acknowledgements

We acknowledge the financial support of International Science Foundation (ISF Grant # MN2000/MN2300) and Russian Foundation of Fundamental Research (Grant No. 93-03-18479).

References

[1] J.H. Lunsford, Langmuir, 5 (1989) 12.

[2] O.V. Krylov, Catal. Today, 18 (1993) 209.

[3] M.Y. Sinev, L.Y. Margolis and V.N. Korchak, Russ. Chem. Rev., 64 (1995) 349.

[4] T. Fang and C. Yeh, J. Catal., 69 (1981) 227.

[5] G.E. Keller and M.M. Bhasin, J. Catal., 73 (1982) 9.

[6] W. Hynsen, W. Bytyn and M. Baerns, Proc. 8th Int. Congress on Catalysis, Berlin, Verlag Chemie, 3 (1984) 581.

[7] K. Asami, K. Omata, K. Fujimoto and H. Tominaga, J. Chem. Soc., Chem. Commun., (1987) 1287.

[8] V.I. Vedeneev, O.V. Krylov, V.S. Arutyunov, V.Y. Basevich, M.Y. Goldenberg and M.A. Teitel'boim, Stud. Surf. Sci. Catal., 82 (1994) 435.

[9] M.Y. Sinev, V.N. Korchak and O.V. Krylov, Kinet. Katal., 28 (1987) 1376.

[10] Y.P. Tulenin, A.A. Kadushin, V.A. Seleznev, A.P. Shestakov and V.N. Korchak, Catal. Today, 13 (1992) 329; Y.P. Tulenin, A.A. Kadushin, V.A. Seleznev, A.P. Shestakov and V.A. Menshikov, Kinet. Katal., 13 (1992) 523.

[11] M.Y. Sinev, G.A. Vorob'eva and V.N. Korchak, Kinet. Katal., 27 (1986) 1164.

[12] V.N. Kondrat'yev, Determination of Rate Constants of Gas-Phase Reactions, Nauka, Moscow, 1971.

[13] J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Nature, 348 (1990) 428.