Selectivity Control by Oxygen Pressure in Methane Oxidation over Phosphate Catalysts

Mikhail Yu. Sinev,*[a] S. Setiadi*[b] and Kiyoshi Otsuka*[b]

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation. Fax: +7 095 938 2156*

[b] *Tokyo Institute of Technology, Tokyo, Japan. Fax: +81 3 3729 0542*

Selectivity shifts from formaldehyde to ethane with oxygen pressure and temperature variation in methane oxidation over phosphate catalysts are evidence for the existence of mutual intermediate and different product selectivities over different catalysts under the same reaction conditions, indicating the participation of the surface in formaldehyde formation.

Extensive studies of methane oxidative coupling into higher hydrocarbons carried out since Fang and Yeh[1] has led to the creation of efficient catalysts for this process[2] and to an improvement of our understanding of the reaction mechanisms.[3,4] However, progress in studies of methane partial oxidation to oxygenates (methanol and formaldehyde) has not been so rapid. High yields of the products were obtained and kinetic and mechanistic studies were carried out for Mo- and V-containing catalysts in the presence of N_2O as oxidant.[5-7] Good results reported for methane partial oxidation by O_2 are not reproducible. Systematic studies of the mechanism of this process, especially in the case of catalysts which do not contain easily reducible cations, have not yet been carried out. Information concerning this type of catalyst such as the nature of active sites, mechanism of reactant activation and product formation pathways is still absent.

Recently the effect of a reversible selectivity switch from CO and ethane to formaldehyde in methane oxidation over MgO has been observed.[8] However, only the total flow rate of reactants was varied, and it was impossible to separate the effects of changes in residence time and in oxygen concentration and to make definite conclusions about the origin of the effect.

The present study was carried out to reveal the main features of methane oxidation over phosphate catalysts and to throw light on possible reaction mechanisms.

Metal phosphate catalysts (denoted as M-P) were prepared by precipitation from aqueous solutions of metal nitrates (Fe, Zn, Zr) and phosphoric acid, followed by drying and calcination in air. Catalyst (0.5 g) was placed into a quartz reactor (inner diameter 7 mm) and stabilized by treatment under reaction conditions (CH_4+O_2+He mixture, 898–998 K) for 2 h. On-line GC-analysis was used to measure the concentrations of reactants and products (H_2, CO, CO_2, C_2 hydrocarbons, methanol and formaldehyde).

The catalytic properties of Fe, Zn and Zr phosphate samples are presented in Table 1. The main products of methane oxidation over all catalysts studied were formaldehyde, ethane, carbon oxides, water and hydrogen. Ethylene was the minor product at higher temperatures and low flow rates. Methanol formation was negligible. The selectivity to formaldehyde decreases with rising reaction temperature, but that to C_2 hydrocarbons increases. Catalytic properties of zirconium phosphates are dependent on the Zr:P ratio and calcination temperature.

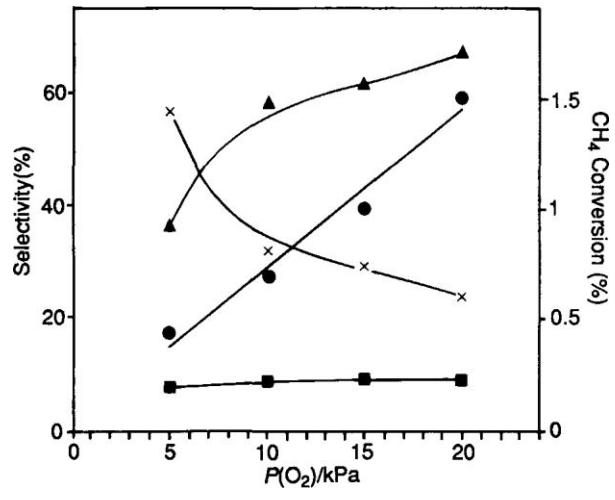

Fig. 1 Catalytic performance of Fe-P with oxygen pressure variation. $T=998$ K; P (CH_4) = 20 kPa. Symbols: ×, HCHO selectivity; ▲, CO selectivity; ■, C_2H_6 selectivity; ●, CH_4 conversion

In the presence of Fe-P catalyst an increase in oxygen partial pressure leads to a decrease in selectivity to HCHO (see Fig. 1) and hydrogen is absent in the reaction mixture. Obviously, the main way of consecutive transformation of formaldehyde over this catalyst is oxidation to CO and water.

Table 1 Catalytic properties of phosphates in methane oxidation (CH_4:O_2:He = 1:1:3, 50 cm^3 min^{-1}, 0.5 g of catalyst)

Catalyst	T/K	CH_4 conversion (%)	Selectivity (%)				
			HCHO	C_2H_6	CO	CO_2	H_2:CO
Fe:P = 1:2	948	0.4	42.2	5.6	52.3	0	0
(calc. 873 K)	973	0.7	35.4	5.9	58.7	0	0
	998	1.5	23.8	9.0	67.2	0	0
Zn:P = 1:2	973	0.4	36.1	26.5	37.4	0	0
(calc. 873 K)	998	0.7	26.0	30.0	41.7	0	0.1
Zr:P = 1:1 (calc. 973 K)	973	2.1	16.3	9.7	68.9	5.1	0.63
Zr:P = 1:1 (calc. 1073 K)	973	1.7	11.0	13.0	72.7	3.3	0.45
Zr:P = 1:0.6	948	0.4	33.6	11.2	55.2	0	0.23
(calc. 873 K)	973	2.0	32.1	12.6	47.5	7.8	0.25
	998	4.0	13.8	16.9	61.9	3.7	0.50

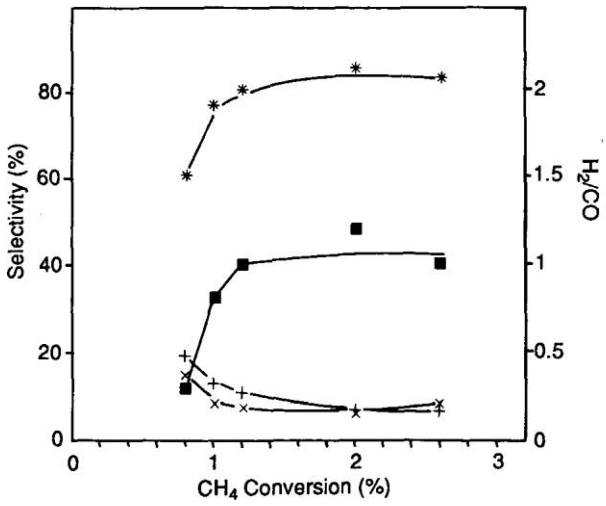

Fig. 2 Selectivity *vs.* CH_4 conversion variations with changing flow rate. $T=973$ K, P (CH_4) = P (O_2) = 20 kPa, Zr:P = 1:1 (973). Symbols: +, HCHO selectivity; ■, H_2/CO; *, CO selectivity; ×, C_2H_6 selectivity

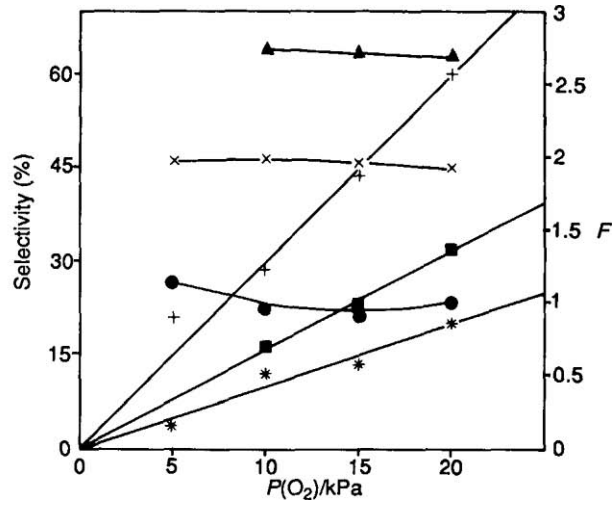

Fig. 3 Total selectivity to HCHO and C_2; $S = S_{HCHO} + S_{C_2}$ and the ratio $F = S_{HCHO}/S_{C_2}$ as a function of oxygen pressure. $T=973$ K; P (CH_4) = 20 kPa. Symbols: + (F) and × (S), Zr:P = 1:0.6 (873); * (F) and ● (S), Zr:P = 1:1 (1073); ■ (F) and ▲ (S), Zn:P = 1:2 (873)

In the case of Zr-P catalysts significant amounts of H_2 are produced. The decrease of conversion at rising total flow rate leads to a change of selectivity to HCHO and CO in opposite directions (see Fig. 2). Partial loss of formaldehyde and relatively high H_2:CO ratios may be caused by HCHO decomposition.[9] The probability of two other ways of hydrogen formation[8] seems to be low: (*a*) thermal decomposition of ethane because of the absence of C_2H_4 in the reaction mixture in most of the experiments and (*b*) steam conversion of CO or methane because of the low concentration of water at high flow rates and the independence of the H_2/CO ratio on temperature below 973K. The selectivity of HCHO and ethane both decrease at decreasing flow rate. Therefore we can suppose that there is no influence of residence time on reaction pathways.

The most relevant feature of the process over Zr-P and Zn-P catalysts is the slight dependence of the total selectivity on formaldehyde and ethane but the high sensitivity of their ratio on oxygen concentration (see Fig. 3). This is an indication of the existence of mutual intermediates for oxygenate formation and oxidative coupling, most likely methyl radicals forming as a result of methane interaction with active sites on the surface[3,4], reaction (1).

$$[O]_s + CH_4 \rightarrow [OH]_s + CH_3 \quad (1)$$

Both gas-phase and heterogeneous steps are considered to have an influence on the final product distribution.[8,10]

In homogeneous gas-phase transformations of CH_3 radicals the equilibrium state in reaction (2)

$$CH_3 + O_2 \rightleftharpoons CH_3O_2 \quad (2)$$

is a key-factor in the product distribution.[11] The selectivity to C_2-hydrocarbons is a function of temperature and oxygen partial pressure but depends only slightly on the rate of radical formation, *i.e.* on activity of the catalyst. The source of oxygenates at temperature below *ca.* 1000 K is reaction (3),

$$2CH_3O_2 \rightarrow HCHO + CH_3OH + O_2 \quad (3)$$

and CH_3O radicals formed in consecutive reactions of CH_3O_2.

If the catalyst surface plays a significant role in reactions of radicals and product formation, the additional factor of selectivity control will be heterogeneous reactions such as (4) and (5).†

$$[O]_s + CH_3O \rightarrow [OH]_s + HCHO \quad (4)$$

$$[\ ]_s + CH_3O \rightarrow [O]_s + CH_3 \quad (5)$$

† Empty brackets [ ] signify oxygen vacancy.

The rate constants for the reactions (4) and (5) and product selectivity under the same reaction conditions should vary depending on the thermochemical properties of the catalyst.[12] High H-atom affinity of active surface oxygen species (high O-H binding energy) will accelerate the formation of HCHO in reaction (4). High values of oxygen binding energies should increase the preference of the coupling reaction. The variations of oxygen pressure will lead to selectivity shifts caused by changing of the state of the surface.

Variations in the HCHO:C_2H_6 ratio from one catalyst to another under the same reaction conditions is taken as experimental evidence for surface-assisted product formation and the significant role of radical-surface interactions[12,13] in methane oxidation.

References

1 T. Fang and C. Yeh, *J. Catal.*, 1981, **69**, 227.
2 K. Otsuka, *J. Japan. Petrol. Inst.*, 1987, **30**, 385; J. S. Lee and S. T. Oyama, *Catal. Rev.-Sci. Eng.*, 1988, **30**, 249; J. R. Anderson, *Appl. Catal.*, 1989, **47**, 177; G. Hutchings, M. S. Scurrell and J. R. Woodhouse, *Chem. Soc. Rev.*, 1989, **18**, 251; *Methane Conversion by Oxidative Processes*, ed. E. E. Wolf, Van Nostrand Reinhold, New York, 1992.
3 J. H. Lunsford, *Catal. Today*, 1990, **6**, 235.
4 M. Yu. Sinev, V. N. Korchak and O. V. Krylov, *Usp. Khim.*, 1989, **58**, 38 (*Rus. Chem. Rev.*, 1989, **58**, 22).
5 M. J. Brown and N. D. Parkyns, *Catal. Today*, 1991, **8**, 305.
6 H.-F. Liu, R.-S. Liu, K. Y. Liew, R. E. Johnson and J. H. Lunsford, *J. Am. Chem. Soc.*, 1984, **106**, 4117.
7 K. J. Zhen, M. M. Khan, C. H. Mak, K. B. Lewis and G. A. Somorjai, *J. Catal.*, 1985, **94**, 501.
8 J. S. J. Hargreaves, G. J. Hutchings and R. W. Joyner, *Nature (London)*, 1990, **348**, 428.
9 M. Yu. Sinev, G. A. Vorob'eva and V. N. Korchak, *Kinet. Katal.*, 1986, **27**, 1164 [*Kinet. Catal.*, (*Engl. Transl.*), 1986, **27**, 1007].
10 H. Zanthoff and M. Baerns, *Ind. Eng. Chem. Res.*, 1990, **29**, 2.
11 M. Yu. Sinev, V. N. Korchak and O. V. Krylov, *Kinet. Katal.*, 1987, **28**, 1376 [*Kinet. Catal.*, (*Engl. Transl.*), 1987, **28**, 1188]; M. Yu. Sinev, V. N. Korchak and O. V. Krylov, *Proc. 9th Int. Congress on Catalysis*, Calgary, 1988, ed. M. J. Phillips and M. Ternan, vol. 2, p. 968.
12 M. Yu. Sinev, *Catal. Today*, 1992, **13**, 561.
13 Y. Tong, M. P. Rosynek and J. H. Lunsford, *J. Phys. Chem.*, 1989, **93**, 2896.

Received: Moscow, 26th August 1992
Cambridge, 1st September 1992; Com. 2/04681D