ELSEVIER

Catalysis Today 42 (1998) 367–370

CATALYSIS TODAY

Partial catalytic oxidation and condensation of methane by oxygen and sulphur

L.P. Didenko*, V.R. Linde, V.I. Savchenko

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russian Federation

Abstract

The methane oxidation by oxygen is carried out on catalytic systems Mo–V–Cu–P–O, W–Pb–B–O and V–Zn–Bi–B–O containing 1% Pt or Pd. The design of reactor makes possible to decrease the deep oxidation rate and leads to increase of oxygenates yield. Thermodynamic analysis of methane and sulphur interaction with calculation of all product concentrations at molar relationship S_2:CH_4 from 0 to 5, temperatures in the range from 750 to 1500 K and pressures from 1 to 100 atm has been carried out. The possibility of interaction between methane and sulphur forming products of partial oxidation and condensation was confirmed experimentally. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxygen; Sulphur; Oxidation

1. Introduction

The high strength of C–H bonds in a molecule of methane leads to high temperature of its interaction and low yield of the products of partial oxidation. The oxygenated products yield can be increased by decreasing deep oxidation rate. This paper presents the reactor for catalytic oxidation of methane by oxygen which design allows to decrease CO_2 and H_2O formation.

Furthermore, partial oxidation and condensation of methane with sulphur is studied. Realization of such reactions will make it possible to produce valuable products from natural gas and sulphur. The thermodynamic calculation of all product concentrations in a wide range of temperatures, pressures and molar ratios S_2:CH_4 have been carried out.

2. Results and discussion

2.1. Catalytic oxidation of methane by oxygen

Methane activation on metallic and oxide catalysts, usually, needs high temperatures. At the same time, there are some compounds, such as Mo–V–Cu–P–O, W–Pb–B–O, V–Zn–Bi–B–O containing 1.0% Pt or Pd which decrease methane activation temperature to 670–560 K. These systems are glass-like alloys and can be deposited on a bed by thin layer.

Reactor used (Fig. 1) represents a thin stainless steel tube (inner diameter – 22 mm, length – 600 mm (2)) equipped with cooling jacket (1) and an upper flange. Stainless steel heater (4) (diameter=12 mm) with Ni–Cr spiral (5) inside (P=1.2 kW) was inserted into the reactor through the flange. A screen, consisting of 12 flattened stainless steel tubes (with 4 mm diameter, wall thickness 0.2 mm) (3) was

---

*Corresponding author.

PII S0920-5861(98)00117-5

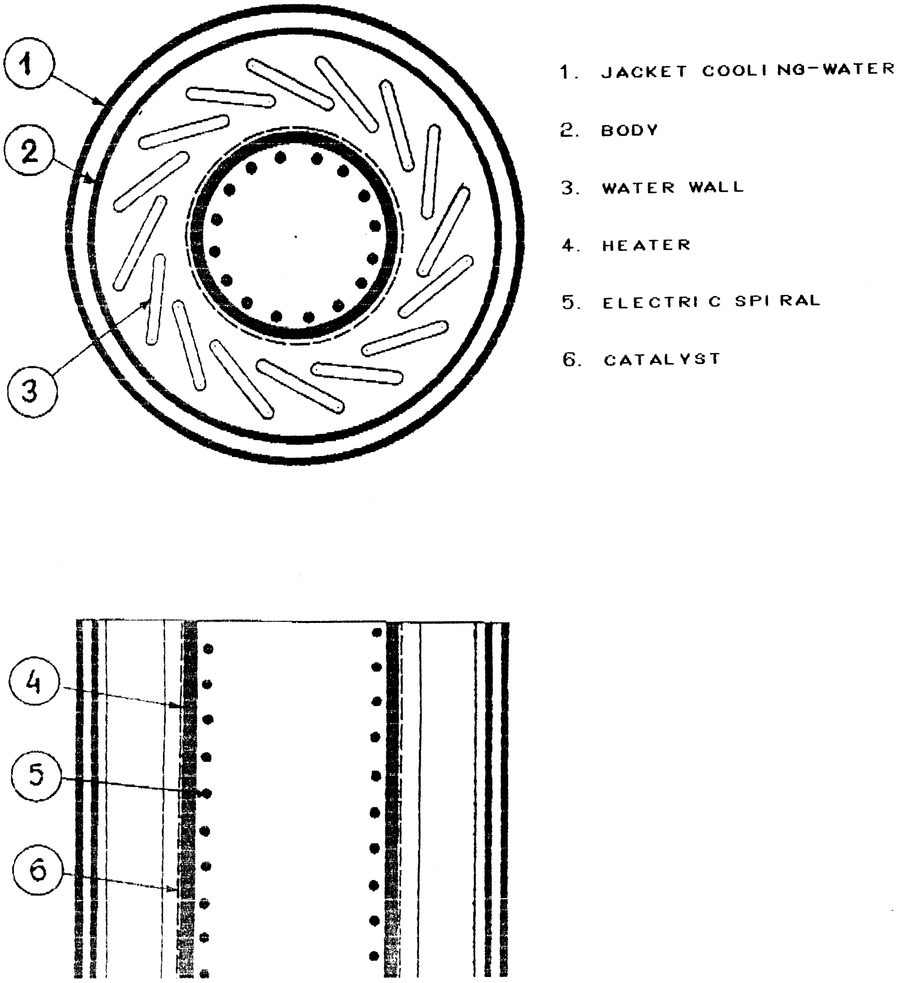

Fig. 1. The design of the reactor.

placed between heater and reactor walls. To prevent radiation action on gas molecules between flat surfaces of screening tubes, the latter were oriented to the surface by a particular angle. Top and bottom of these tubes were connected to ring-shape collector of coolant supply. Catalyst obtained as paste was deposited on Si-fibre cloth which covered the heater (6). Temperature of the catalyst layer was measured by three thermocouples. Free volume of the reactor was 180 cm^3.

5 l of methane, 10 l of oxygen and 10 l water vapour mixture per 1 h was passed through the reactor. Temperature of catalyst was 690 K. Water at T=293 K was used as a coolant. Mixing of reaction mixture was performed by a pulse pump with efficiency 350 l/h. Total conversion of methane under these conditions was as high as 30%, formaldehyde–methanol mixture selectivity – 8.5%. Formation of carbon dioxide and water was only observed without cooling.

2.2. *Partial oxidation and condensation of methane by sulphur*

Oxidation of methane with a participance of other oxidants, such as sulphur is of some interest. Deep oxidation of methane by sulphur with production of CS_2 is well known. The reactions of partial oxidation of methane by sulphur also could be useful for industrial applications.

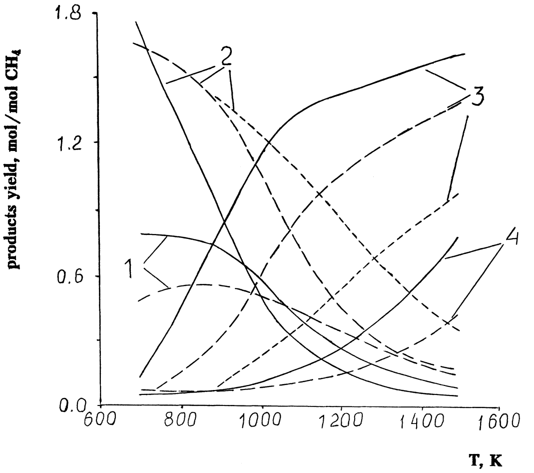

Fig. 2. The dependence of methane conversion and deep oxidized products yield on conditions: S_2:CH_4=0.1:1:1; (1) CS_2, (2) H_2S, (3) H_2, (4) methane conversion; (———) 1 atm; (– – –) 10 atm; (- - -) 100 atm.

In this paper a capability of sulphur to oxidize CH-bounds of methane into partial oxidation and condensation products is considered. Similar reactions of sulphur with hydrocarbons, which contain two or more atoms of carbon are well known.

By using a technique described in [1] thermodynamically possible yield of all products was determined. A quasi-equilibrium process without C formation was simulated. (Taking C formation into account leads to graphite as a main equilibrium product.)

The influence of temperature and pressure on the yield of reaction products and conversion of methane is shown in Figs. 2 and 3. The increase in temperature in the range 750–1500 K leads to increase of methane conversion, decrease of CS_2 and H_2S yield and increase of H_2 content in the mixture obtained (Fig. 2).

The increase in pressure leads to decrease of methane conversion and shifts the maximum yield of partial oxidation and condensation products (POCP) to the higher temperature region (Fig. 3). The highest content of methanethiol is achieved in the range of pressure from 1 to 100 atm at temperature from 900 to 1100 K. The yield of ethylene increases significantly up to 1000–1300 K and decreases at higher temperatures. The increase of C_2H_2 content in mixture begins at $T\sim1300$ K and it decreases when the pressure increases.

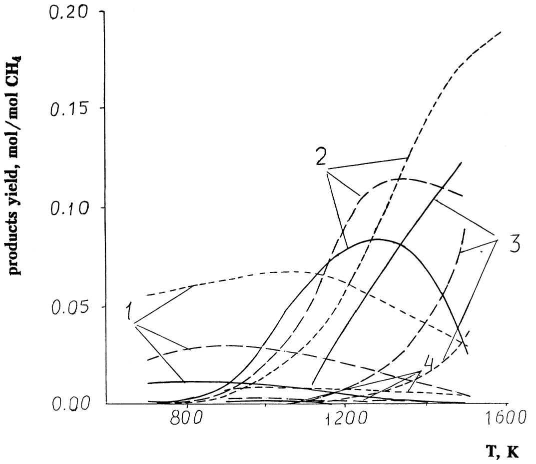

Fig. 3. The dependence of the POCP yield on reaction conditions: S_2:CH_4=0.1:1:1; (1) C_2H_6; (2) C_2H_4; (3) C_2H_2; (4) CH_3SH; (———) 1 atm; (– – –) 10 atm; (- - -) 100 atm.

The increase in ratio S_2:CH_4 leads to increase of methane conversion, particularly into CS_2 and H_2S, at the same time the yield of POCP decreases.

One may suppose that the reaction performance in the presence of an ideal catalyst which does not activate the formation of C and CS_2, olefin hydrocarbons C_2–C_3 might be obtained as basic products of the reaction (Fig. 4). The greatest yield of ethylene

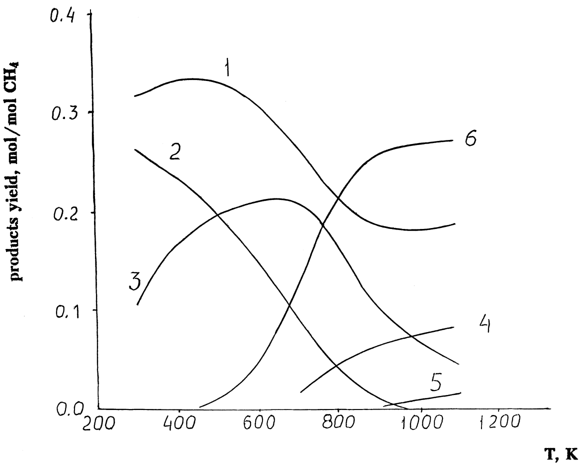

Fig. 4. POCP yield and methane conversion without C and CS_2 formation: P=10 atm; S_2:CH_4=0.1:1:1; (1) methane conversion, (2) C_3H_8; (3) C_2H_6; (4) C_4H_2; (5) C_2H_2; (6) C_2H_4.

(0.25–0.28 mol/mol CH_4) is achieved at temperature from 900 to 1100 K.

Thus, calculations confirm the thermodynamic possibility of interaction of methane with sulphur yielding POCP.

Experimental study of reaction of methane with sulphur was directed mainly on formation of CS_2 [2]. Hydrocarbons containing two or more atoms of carbon were produced by the reduction of CS_2 by hydrogen [3] or interaction of methane with COS [4]. Performance of oxidative condensation of methane on some metal sulphides at 1100–1200 K yields C_2- and C_3-olefines in accordance with the following scheme [5]:

$$\mathrm{Me}_n\mathrm{S}_m \rightarrow \mathrm{Me}_n\mathrm{S}_{m-1} + 0.5\mathrm{S}_2$$

$$\mathrm{CH}_4 + 0.5\mathrm{S}_2 \rightarrow [\mathrm{CH}_2] + \mathrm{H}_2\mathrm{S}$$

The proposed scheme is possible because the metal sulphides used in [5] decompose at high temperatures forming sulphur [6].

We studied the interaction of methane with sulphur vapour in flow regime at temperature from 900 to 1100 K and contact time 0.7–7 s in the presence of MoS_2, FeS_2 and PbS. The formation of hydrocarbons was observed in the presence of MoS_2 and FeS_2 (but FeS_2 decomposes and becomes low-active under heating). For reaction on MoS_2 the methane conversion is 3.1%, the yield of CH_3SH, C_2H_5SH, C_2H_4+C_2H_2, CS_2 is 11.9%, 53.6%, 20.2%, and 14.4%, respectively (1073 K, contact time is 0.7 s). The increase of contact time leads to increase of methane conversion and the content of deep oxidized products (CS_2, H_2S) and to decrease the yield of hydrocarbons and mercaptanes. Changing the temperature in the range 1100–900 K leads to reduction of methane conversion and the yields of all products.

Thus, our calculations and experimental data obtained point out on a principal possibility of partial oxidation and condensation of methane by sulphur.

References

[1] A.G. Merzhanov, M.M. Kitain, U.I. Goldshleger et al., Doklady AN SSSR 237 (1977) 391.
[2] A.A. Peliks, B.S. Aranovich, Chemistry and Technology of CS_2, Khimiya, Moskva, 1986.
[3] C.D. Chang, US Patent 4 543 434 (1986).
[4] C.D. Chang, US Patent 4 864 073 (1990).
[5] S.D. Kusch, V.I. Savchenko, Izv. AN SSSR, ser. Khim. N4 (1989) 976.
[6] G.B. Samsonov, S.B. Drozdova, Sulfides, Metallurgia, Moskva, 1972.