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Catalytic combustion of lean methane–air mixtures

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Abstract

Catalytic combustion of lean methane–air mixtures was studied on supported iron oxide and platinum monolith catalysts. Flameless catalytic combustion was investigated in the temperature range 600–900°C, GHSV up to 10 000 h^{-1}, and methane concentration in initial gas mixture 1–9 vol%. It was shown that under certain process conditions complete combustion of methane at ~4.5 vol% inlet methane concentration occurs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; Catalytic combustion; Methane; Lean mixture

1. Introduction

Both conventional and catalytic methane burners usually operate at a nearly stoichiometric CH_4/O_2 ratio to achieve a high fuel efficiency and output [1]. On the other hand, the problem of utilization of the BTU value of methane in a lean mixture with air, e.g. in gas emissions from coal mines, is an urgent problem for catalytic combustion application. It is necessary to study oxidation of lean methane–air mixtures both to produce heat and to solve environmental problems.

Evidently, conventional flame burners do not process efficiently lean methane–air mixtures. In literature various catalytic systems for effective total oxidation of methane are described [2–4]. In the present work we studied the concentration and temperature regions for stable performance of methane catalytic combustion in lean mixtures over iron oxide and platinum catalysts on ceramic multihole supports.

2. Experimental

Special demands are imposed on the catalysts for fuel combustion. They must resist thermal and mechanical shocks, exhibit high activity, and their preparation must be harmless to environment.

2.1. Catalytic support

A multihole plate ceramic support was prepared from natural raw materials of the Siberian region via a wasteless procedure. Initial materials for the support production were clay, kaolin, talcum, tremolite, and active carbon. Main support components are silica, alumina, magnesia, and the admixtures of calcium oxide, iron oxide, and sodium oxide. To obtain the desired texture parameters organic additions were introduced. The raw paste was molded as multihole 80×72×11 mm plates, hole diameter being 1.1 mm, hole density being 26 holes/cm^2. After drying the plates were calcined at 900°C. The support has a 3–5 m^2/g specific surface area and a 0.32 cm^3/g pore volume. Weight of catalytic plate is 80 g.

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2.2. Catalysts

Using thus prepared supports we synthesized two types of catalysts, iron oxide and platinum.

Iron oxide catalysts were prepared by incipient wetness impregnation of the above support using Fe^{3+} aqueous solutions of various concentrations. The iron content ranged from 1.8 to 9.3 wt%.

We prepared platinum catalysts in two ways:

1. impregnating the support with aqueous H_2PtCl_6, the Pt content in the catalyst being 0.3 wt%, and
2. spraying aqueous H_2PtCl_6 of different concentrations over either one side (inlet or outlet) or both sides of a ceramic plate, Pt content in thus prepared catalysts being 6.6–144 mg.

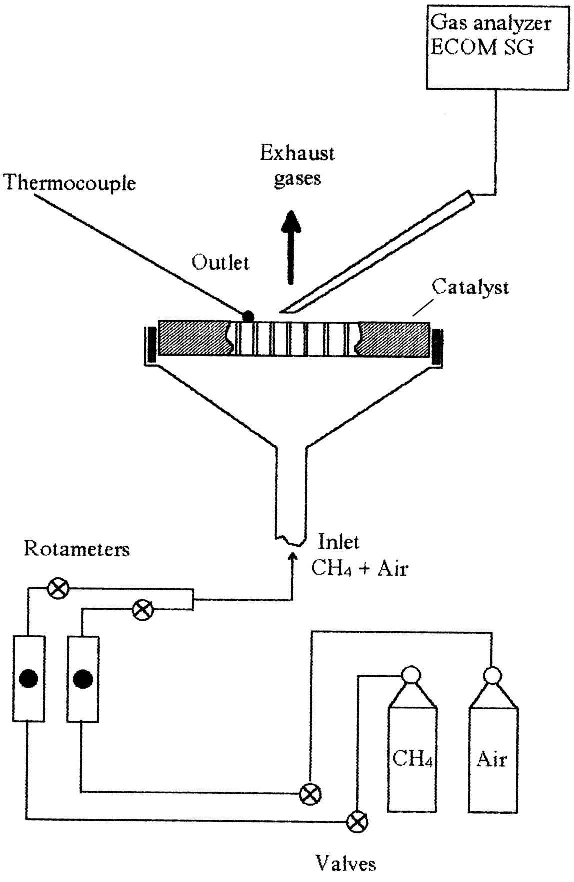

Fig. 1. Scheme of experimental set-up.

Table 1
Characteristics of platinum supported catalysts

Catalysts	Pt content in solution (mg Pt/ml)	Pt localization side	Pt content (mg on one plate)
CP-77	1.6	Outlet part	6.6
CP-78	1.6	Inlet part	6.6
CP-79	1.6	Both sides	3.3×2
CP-80	18	Inlet part	45
CP-81	18	Inlet part	144

After coating the catalysts were dried at 120°C and calcined at 500°C.

Characteristics of the Pt-catalysts are presented in Table 1. Catalyst activity in methane oxidation was measured by a flow circulation set-up at 520–560°C and characterized by the rate of methane oxidation at 540°C and stationary methane concentration of 0.5 vol%. Inlet methane content was 1 vol%.

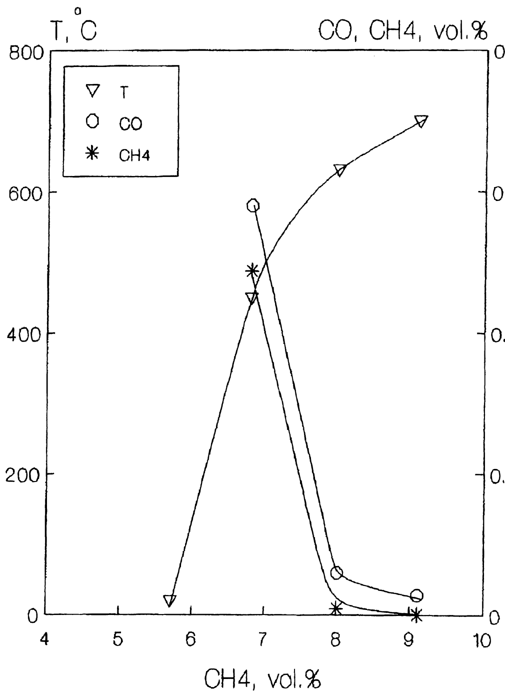

Fig. 2. Temperature of radiant surface and content of CH_4 and CO in flue gas versus methane concentration in initial gas mixture fed to the multihole ceramic plate catalyst (2.4 wt% Fe, methane and air=440 l/h).

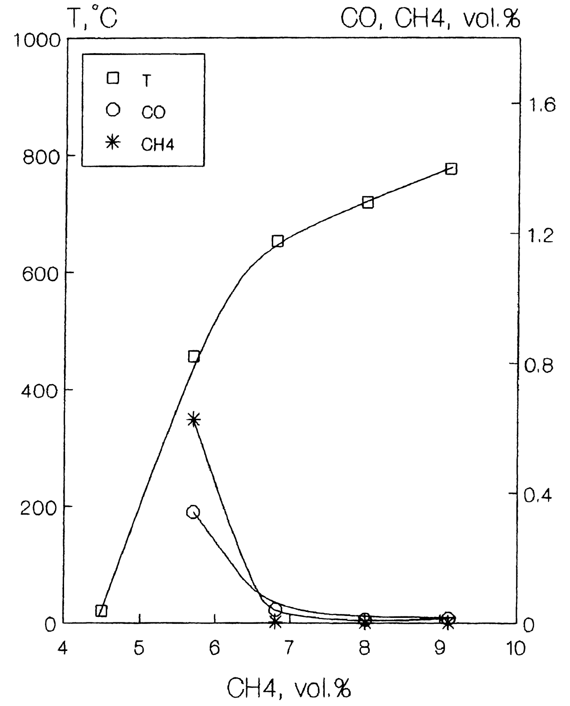

Fig. 3. Temperature of radiant surface and content of CH_4 and CO in flue gas versus methane concentration in initial gas mixture fed to the multihole ceramic plate catalyst (6.6 mg Pt on inlet side of plate of catalyst, weight of plate 80 g, CH_4+air=440 l/h).

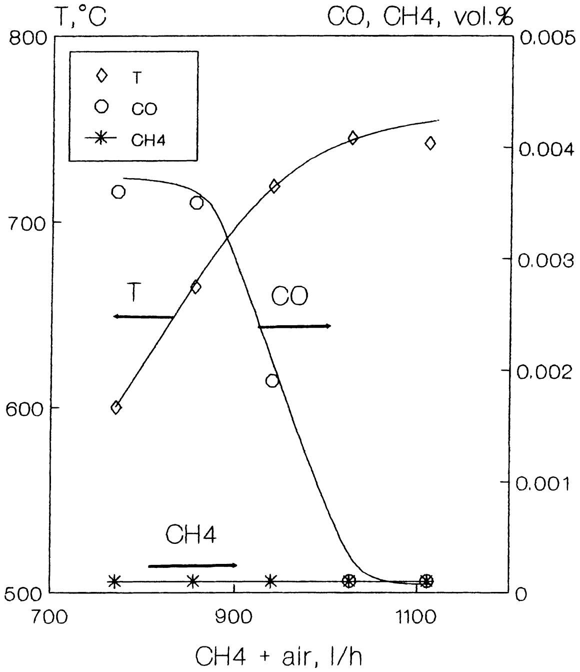

Fig. 4. Combustion efficiency of methane versus methane+air mixture feed (methane content 5.8 vol%, catalyst 45 mg Pt on inlet side of multihole ceramic plate, weight of plate 80 g).

Full size synthesized catalysts were tested within a special bench at 20–900°C and GHSV up to 10 000 h^{-1}. Inlet methane concentration was 1–9 vol%. Concentration of CO and CH_4 in exhaust was analyzed by GC with an accuracy of 10^{-3} vol% and of CO, NO, NO_2, SO_2 with ECOM-SG-Plus with a 1 ppm accuracy. Catalyst efficiency was estimated by calculating the conversion of CH_4 to CO_2 and CO.

3. Results and discussion

Physico-chemical methods (XRD, chemical analysis, TPR, ESDR) proved that iron is present as phases Fe_3O_4, α-Fe_2O_3, iron(III) oxide associates and as isolated ions Fe^{3+} in the aluminasilicate frame.

Previously [5] in experiments on CH_4 oxidation in a flow-recycle reactor we showed the existence of a linear dependence of the rate of methane oxidation on the total iron content and especially on the dispersity of iron in the case of supported catalysts. Dispersity of iron oxides was defined as $D=N_s/N_v$ (%), where N_s and N_v are numbers of atoms of iron on the surface and in the volume of the catalysts, respectively. The reaction order with respect to methane ranges from 0.7 to 1.0, the activation energy being 26–30 kcal/mol agrees well with the literature data [6].

On the basis of these experiments we selected optimum composition and supporting conditions to obtain samples of the highest activity. Samples CP-2.4 and CP-4.4 were chosen for bench testing. Numbers in the names of catalysts designate the content of iron in catalysts samples in wt%.

3.1. Catalyst testing

The aim of bench scale catalyst tests is to determine the conditions of most stable methane combustion. Fig. 1 represents a scheme of the experimental set-up. For this purpose we varied the content and the type of active component, the place of its localization, and the

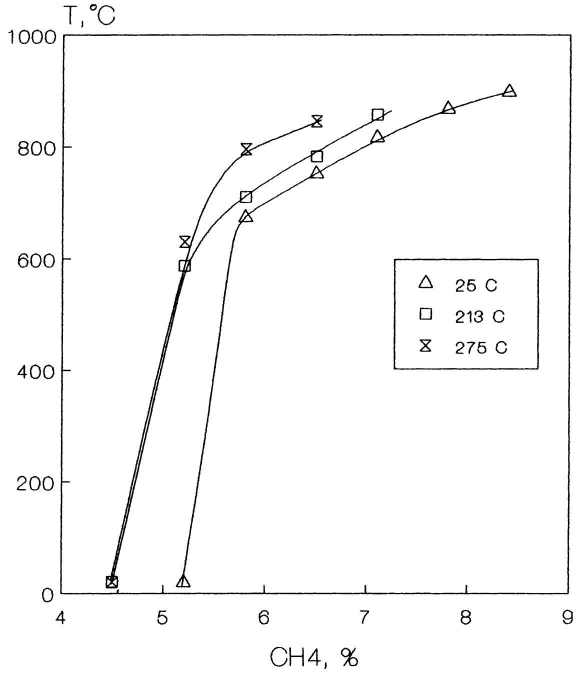

Fig. 5. Combustion temperature and stability at different preheating temperatures of methane+air mixture versus content of methane in mixture (catalyst Fe/ceramic, feed 770 l/h).

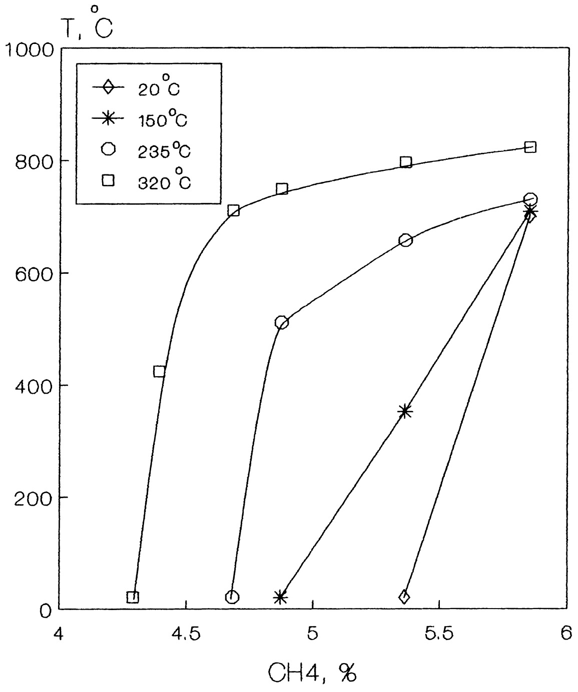

Fig. 6. Combustion temperature and stability at different preheating temperatures of methane+air mixture versus content of methane in mixture (catalyst Pt+Fe_2O_3/ceramic, feed CH_4+air= 1026 l/h).

inlet gas mixture temperature. Preliminary experiments indicated that for stable methane combustion the temperature should not be less than 700°C. Fig. 2 represents the results for the CP-2.4 sample under standard conditions: methane–air mixture feed – 440 l/h, methane concentrations up to 9.0 vol%. Methane conversion was complete, when the catalyst surface temperature was 700°C.

However, as the methane concentration falls below 8.1 vol% the catalyst surface temperature decreases sharply, and the methane and CO concentration at the outlet increase. When a Pt-catalyst is used instead of the iron oxide, a high efficiency is maintained at methane concentrations down to 6.8 vol% and 620°C (Fig. 3). Experiment shows that platinum deposited on the inlet side of plate is more efficient. Apparently, reaction initiation in this case occurs at the inlet of the cylindric channels.

As the heat produced by methane oxidation in leaner mixtures is insufficient to attain the needed temperature (700–800°C), we tried to compensate the heat deficit by increasing volume velocity and imposing adiabatic conditions by variation of inlet mixture parameters. Fig. 4 represents plate surface temperature versus air–methane GHSV. Complete combustion of methane in a mixture of a concentration of 5.8 vol% CH_4 occurs at 1100 l/h.

Another way to increase the catalyst temperature is preheating of the inlet mixture. Results of preheating are presented in Figs. 5 and 6. It is possible to achieve the required temperature of 800–850°C on the catalyst plate at a methane concentration of 4.5 vol% by using a platinum catalyst and preheating the inlet gas flow at 320°C; the CO content being less than 20 ppm. In general the range of methane sustainable combustion can be extended by choosing an efficient catalyst and appropriate combustion conditions.

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