CERAMIC FOAM IN CATALYTIC COMBUSTION OF METHANE*

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Catalytic combustion of methane has been studied in the presence of catalysts supported on ceramic foams. Low concentrations of NO_x (in the range of 5 – 50 mg m^{-3}) were observed with all catalysts used. Concentrations of CO depended strongly on the type of the catalyst, its composition, methane throughputs and varied from 4 400 to 0 mg m^{-3}. Minimum CO concentration (0 – 8 mg m^{-3}) was gained with 0.04% Pt on ceramic foam modified with both alumina Al_2O_3 and lanthana La_2O_3.

Catalytic combustion of methane or natural gas is a very important process in which the formation of nitrogen oxides can be eliminated[1] in comparison with the process of flame combustion. The advantage of the catalytic combustion is it can be carried out in a wide range of methane concentration in air and at relatively low reaction temperatures (compared to flame combustion)[1–3].

Catalytic combustion of lean fuel mixtures at low temperatures is assured only by highly active catalysts, for example supported platinum or palladium. According to Prasad[2] palladium is more active in oxidation of CO, methane and olefines while platinum in oxidation of paraffines with the chain longer than C3.

Geometric form of the combustion catalyst is very important especially in ceramic burners. They are usually prepared in the form of monoliths as they show low pressure drop. In the course of methane combustion, reaction rate of oxidation of methane is very high and thus, mass transfer from the gas phase to the catalyst surface should be very fast. Rate of the mass and heat transfer could be positively affected by a great extent of turbulence in the catalyst channels. Ceramic foams with their nonuniform channels of various diameters, shapes and paths, i.e. with their irregular porous structures could fulfill this requirement. Mixing of reaction mixture in the foam is, very probably, more perfect than in monoliths and thus, combustion of methane can proceed

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more entirely. Inui and coworkers[4] have already used the ceramic foams as the supports of catalysts for the combustion of methane.

The aim of this work was to find out how perfect is the catalytic combustion of methane especially with regard to the NO_x and CO concentrations in flue gases produced by the catalytic ceramic foam burner. In the course of experiments the foam was modified with different active admixtures (alumina, lanthana, palladium and platinum in various combinations).

EXPERIMENTAL

Catalysts and Chemicals

The ceramic foam (support) was supplied by Chemopetrol Litvinov, (The Czech Republic). Its bulk density was 560 kg m^{-3} and external surface area 650 m^2 m^{-3}. Diameter of the channels was about 4 mm.

The support samples of a dimension 5 × 5 × 2 cm were covered with a sol of aluminum hydroxide or with a sol of aluminum hydroxide containing lanthanum nitrate. Alumina sols used in the catalyst preparation were prepared in such concentrations in order resulting amounts of alumina of 10 wt.% on the support were assured. Ratio of the alumina and lanthana amounts in the catalysts was 20. After the calcination at 800 °C for 2 h the samples were impregnated with a solution of chloroplatinic acid or palladium chloride to the requested amount of Pd or Pt. The survey of the catalysts prepared is given in Table I.

TABLE I
The NO_x concentrations (mg m^{-3}) and the CO concentrations (mg m^{-3}) in the effluents for two different throughputs of methane Q_1 (<200 l h^{-1}) and Q_2 (>200 l h^{-1}). Air excess $\lambda \approx 1.6$

No.	Composition	NO_x	CO	
			Q_1	Q_2
1	Foam (F)	7 – 10	250	60
2	F + Al_2O_3 (A)	5 – 12	200	60
4	F + A + 0.01% Pd	5 – 13	50 – 100	80
3	F + A + La_2O_3 (La)	5 – 11	≈500	≈40
5	F + A + La + 0.01% Pd	7 – 12	50 – 100	–[a]
9	F + A + La + 0.04% Pd	8 – 16	20 – 30	20 – 30
6	F + A + La + 0.2% Pd	7 – 15	50 – 80	15 – 25
8	F + A + La + 0.04% Pt	9 – 18	0 – 8	0 – 8
7	F + A + La + 0.2% Pt	7 – 13	30 – 80	0 – 20
10	Monolith + A + 0.05% Pt	8 – 12	4 – 8	–[a]

[a] Not determined.

Apparatus

The study of methane oxidation was carried out in a laboratory stainless steel burner (Fig. 1). Gas mixtures fed into the burner were obtained by mixing of natural gas from supply-line and air (central laboratory compressed air circuit) in appropriate flowrate proportions controlled by valves and measured by means of rotameters. Temperature of the reaction mixture entering the catalyst was measured by Pt–PtRh thermocouple.

The reaction mixtures leaving the burner were analyzed for NO_x, CO, CO_2, O_2 by gas analyzer IMR 3000P (Germany). Products other than cited before were not detected.

RESULTS AND DISCUSSION

In the presence of the ceramic foams modified by active components (Al_2O_3, La, Pd, Pt), variations in the amount of NO_x and CO in the products of methane combustion were determined for various oxygen-to-methane ratio, methane throughputs and time.

NO_x Concentration in the Combustion Products

Changes in the NO_x concentrations in the flue gases of methane combustion with the pure ceramic foam and the foams containing alumina or alumina and lanthana are shown as a function of the air excess λ in Fig. 2. Similar dependence of the NO_x concentration on λ for the catalysts containing various amount of precious metals, palladium or platinum is depicted in Fig. 3. No difference in the NO_x concentrations was observed with the pure ceramic foam and foams comprising noble metals. It indicates no catalytic reaction between nitrogen and oxygen in the course of methane combustion.

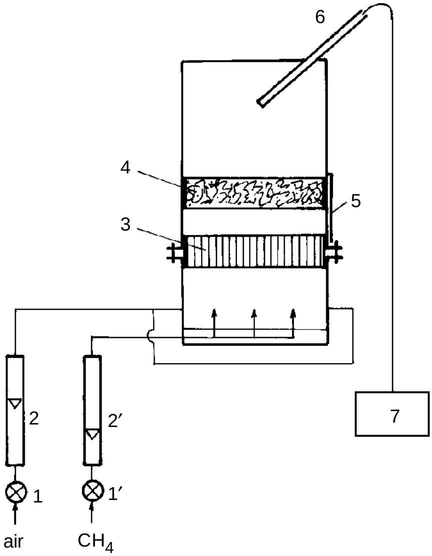

FIG. 1
Scheme of the apparatus: 1, 1′ valves, 2, 2′ rotameters, 3 monolith, 4 catalyst, 5 mica window, 6 tube of analyzer, 7 analyzer IMR 3000P

For all catalytic materials, the NO_x concentration monotonously decreased with increasing oxygen-to-methane ratio. Evidently, with increasing excess of air in the reaction mixture reaction zone temperature decreases as increasing amount of heat is carried away from the reaction zone. Theoretical adiabatic temperatures of the flue gases as a function of λ (Fig. 4) confirm the idea. Since the NO_x concentration in the flue gases is an exponential function of reaction temperature[5], ability of advanced burners comprising ceramic foams, monoliths or other solid materials to combust methane with high excess of air, i.e. with relatively low temperature, is very advantageous.

CO Concentration in the Combustion Products

In the combustion products of methane obtained with all catalysts, the CO concentrations moved in the range of units to thousands mg m^{-3}. In comparison with the NO_x concentration the CO concentration was not so simply dependent on the excess of air λ in the reaction mixture.

An example of the dependence of the CO concentration on the excess of air λ is given in Fig. 5. It shows two sets of points: The first one was obtained with the ceramic foam modified with alumina and lanthana (sample 3), the other with the same catalyst containing, in addition, 0.04 wt.% of Pt (sample 8). In both cases the dependencies show minimum in the CO concentration at the value of λ about 1.5 – 1.6. The existence of such a minimum is known from the literature[6] and can be explained in a simple way:

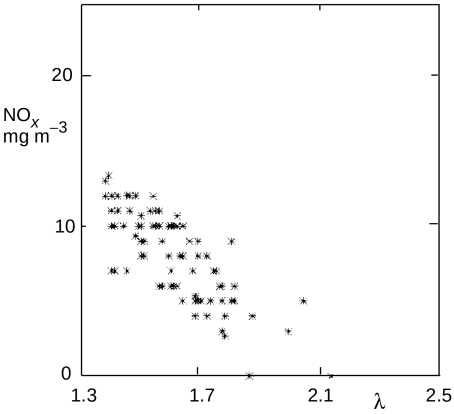

FIG. 2
Dependence of the NO_x concentration (mg m^{-3}) in the flue gases on the excess of air λ for the pure foam, the foam with alumina and the foam with alumina and lanthana

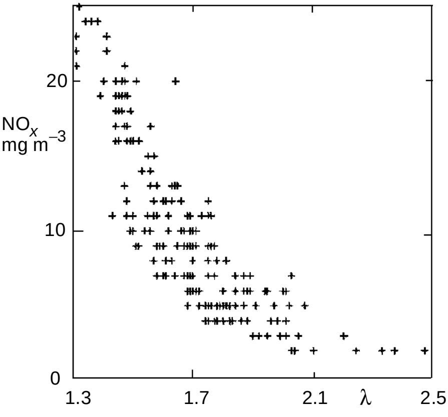

FIG. 3
Dependence of the NO_x concentration (mg m^{-3}) in the flue gases on the air excess λ for ceramic foams modified with alumina, lanthana and various amount of palladium or platinum (catalyst samples Nos 4 – 9)

With an increase of the air excess above λ = 1 the oxidation rates of methane and CO rise simultaneously due to higher content of oxygen in the reaction mixture. However, at the specific point (at the λ value between 1.5 – 1.6 in our case) the temperature of the foam surface begins to fall down as a result of higher heat removal by reaction gases. Consequently, the degree of methane combustion and CO oxidation to CO_2 decreases and therefore, the CO concentration in the flue gases increases.

Figure 5 also clearly documents the difference between the catalyst containing precious metal and the catalyst without it. Platinum present in the catalyst sample affects composition of combusted gases in two aspects: Absolute values of all CO concentrations are two order of magnitude lower and, in addition, the region of the minimum CO concentrations becomes broader. The catalytic burner is able to combust methane in a broader range of air excess keeping the CO concentration low enough. Especially important is the extension of the low CO concentration region in the direction of lower values of the air excess. In such a case burners have not to be equipped with extra efficient parts, namely fans.

Pure ceramic foam used in the catalytic burner showed substantially higher values of the CO concentrations (from 1 500 to 55 mg m^{-3}) in dependence on the air excess λ and throughputs of methane. At low methane throughputs (<200 l h^{-1} = 75 W cm^{-2}) the lowest CO concentration determined in the combustion products was about 250 mg m^{-3} at λ ≈ 1.6. At higher methane throughputs (>200 l h^{-1}) the CO concentration decreased

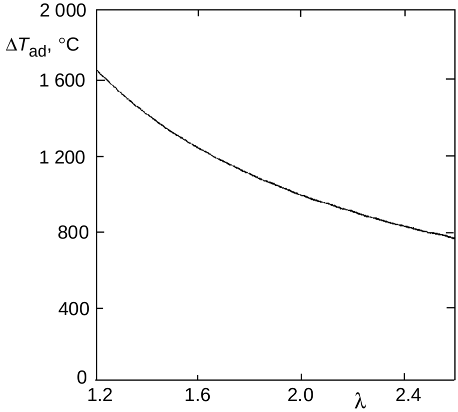

FIG. 4

Dependence of the theoretical adiabatic temperature, ΔT_{ad} (°C) of methane combustion on the air excess λ

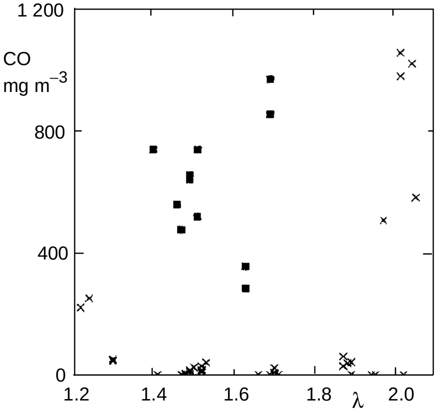

FIG. 5

Dependence of the CO concentration (mg m^{-3}) in the flue gases on the excess of air λ. Catalyst: ■ the ceramic foam with alumina and lanthana. x the ceramic foam with alumina, lanthana and 0.04 wt.% of Pt. Throughput of methane <200 l h^{-1}

and reached the values of 55 mg m^{-3}. It is evident that higher quantity of the methane combusted caused greater amount of heat released which manifested itself in an increase of the surface temperature of the ceramic foam and simultaneously, in an increase of the degree of methane and CO oxidation.

Comparison of Efficiency of Modified Ceramic Foams

In view of the fact that the CO concentration in the flue gases depends on the air excess used in the combustion in a great extent, the combustion efficiencies of various modification of the ceramic foams (with respect to the CO concentration) were compared at the same air excess, namely at $\lambda = 1.6$. The CO concentration determined in the flue gases leaving the combustor with the ceramic foams modified either by alumina, by alumina and lanthana, or by alumina and lanthana with palladium or platinum are shown in the Table I. The results in the table are divided into two groups differing in the methane throughput, the first one being lower than 200 l h^{-1} and the second higher than 200 l h^{-1} of methane. (It was already mentioned that 200 l of methane per hour represents burner capacity = 75 W cm^{-2}.)

It could be seen from Table I that with the ceramic foam covered with alumina (sample 2) the concentration of CO in the flue gases was slightly lower (200 mg m^{-3}) at the lower throughputs in comparison with the results obtained on the uncovered ceramic foam (250 mg m^{-3}). The reason for such findings is apparently in the slight raise of the specific surface area of the foam after covering it by the alumina. Even at high temperatures occurring in the burner (≈1 150 °C) the surface of the solid phase takes part in oxidation. Participation of the solid surface in the methane oxidation has been mentioned by Pfefferle and Pfefferle in their paper[6] dealing with catalytic combustion of methane. When the throughput of methane was increased above 200 l h^{-1} the concentration of CO droped to 60 mg m^{-3}; however, similar data have been achieved when the uncovered foam was used in the burner. It is probable that the alumina covering the foam surface sintered due to high temperatures and therefore, the effect of its larger surface area in the combustion of methane became extinct.

When a small quantity of palladium (0.01 wt.%) was applied on the ceramic foam covered by alumina (sample 4), the CO concentration in the flue gases slightly decreased (compared to the catalyst without precious metal). The decrease can be unambiguously assign to the effect of palladium which was the support impregnated with.

It has been already mentioned that alumina supported on the ceramic foam is not sufficiently stable under the high temperatures of methane combustion in the burner (1 100 – 1 200 °C).

Under the high temperatures used crystallographic structure of alumina changes and its surface area as well. That is why it is recommended to stabilize[7] alumina by addition, for example, of alkaline-earth metals oxides or of rear-earth metals oxides. Therefore, we added 5 wt.% of lanthana to alumina for improvement of its thermal stability.

With the ceramic foam modified in this way we achieved the CO concentration of about 500 mg m^{-3} at low methane throughputs (<200 l h^{-1}) and the CO concentrations about 40 mg m^{-3} at high methane throughputs (>200 l h^{-1}). At low methane throughputs, temperature of the catalyst surface was not evidently high enough to ensure perfect combustion of methane and CO. Low amount of palladium (0.01 wt.%) supported on the ceramic foam with alumina and lanthana decreased the CO concentration in flue gases to the level identical with that one achieved at the catalyst without lanthana.

A decrease of the CO concentration in flue gases (to 20 – 30 mg m^{-3}) was observed when palladium concentration in the ceramic foam containing alumina and lanthana was increased to 0.04 wt.%. The change of the throughputs of methane did not lead to the difference in the CO concentrations of flue gases.

Further increase of palladium concentration in the identical ceramic foam to 0.2 wt.% did not manifest itself positively in the CO concentration decrease. The reason was, very probably, in a sintration of palladium particles of larger dimensions located on the surface of alumina which can be supposed at more concentrated metal catalysts.

Platinum present in the catalyst showed substantially higher efficiency in the oxidation of methane, i.e. in decresing of the CO concentration, than palladium. At low platinum loading (0.04 wt.%) the CO concentrations in the flue gases were very low and moved in the range of 0 – 8 mg m^{-3} not only for lower throughputs of methane but even for high burner output.

High concentration of platinum in the catalyst (0.2 wt.%) did not have any positive effect on the methane combustion as the CO concentration in the flue gases increased to 30 – 80 mg m^{-3} at low methane throughputs and to 0 – 20 mg m^{-3} at throughputs of methane higher than 200 l h^{-1}. Similarly to the case of palladium, sintration of platinum particles dispersed on the catalyst surface obviously proceeded. Loss of platinum by evaporation as a result of high reaction temperatures could be another reason of the catalyst activity decrease.

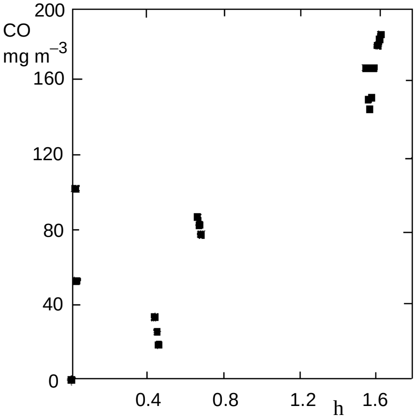

FIG. 6
The CO concentration (mg m^{-3}) in the flue gases as a function of time (h). Catalyst: Foam + alumina + lanthana + 0.04 wt.% Pd

Catalyst Deactivation

Hypothesis that the catalysts containing precious metals deactivate in the course of methane combustion was analyzed in detail with the 0.01 wt.% of Pd catalyst. Figure 6 shows the dependence of the CO concentration in the combustion products (air excess $\lambda \approx 1.75$) on time. The dependence shows a distinct increase of the CO concentration with time that documents successive decrease of the catalyst activity. In addition to the sintration of palladium particles mentioned above, deactivation of the catalyst can be caused by volatilizing of palladium from the catalysts surface as a result of high temperatures achieved during methane combustion (1 100 – 1 240 °C).

Comparison of the Effect of Ceramic Foam and Monolith

It was interesting to compare behaviour of the catalysts prepared on the ceramic foam and a monolith. From Table I it is obvious that the monolith containing approximately the same concentration of platinum as the catalyst prepared on the ceramic foam (sample 8) could oxidize methane to the same level of the CO concentration in the combustion products as the catalyst prepared on the ceramic foam. However, distinct difference between the two catalysts were observed in the maximum throughputs of methane which could be combusted. In case of the use of the ceramic foam it was possible to combust two times higher amounts of methane than in case of the monolith without escaping of the hot zone from the space of the ceramic foam.

CONCLUSIONS

Experimental study showed substantial effect of the ceramic foam and the catalysts based on it on the concentrations of the pollutants emitted from the burners of methane. The NO_x concentration decreased exponentially with the air excess and was practically independent on the catalyst composition.

The CO concentration reflected the presence of active components in the catalysts much more considerably. While the CO concentrations of about 250 mg m^{-3} and more (at low methane throughput) were observed in the presence of pure ceramic foam, the CO concentrations of 5 – 10 mg m^{-3} were registered with the most catalytically active material containing 0.04% Pt in a large scale of the air excess λ (from 1.4 to 2.0). Palladium showed worse catalytic activity than platinum: In average, the CO concentration moved in the range of 30 to 80 mg m^{-3}.

Investigations carried out in this work showed that it is necessary to concentrate an effort on the study of active catalytic materials which will be sufficiently stable at the high temperatures of combustion. Perovskites of the chemical formula ABO_3 (in which A means rare-earth metal and B metal of the VIIIth group) could be potentially useful materials.

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