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METHANE REMOVAL
FROM COAL MINE VENTILATION AIR
OVER MONOLITHIC PALLADIUM CATALYSTS
IN A LARGE LABORATORY INSTALLATION**

1. Introduction

Methane is typically emitted by gas transport systems, crude oil and earth gas refining installations. The emission of methane is an inherent part of bituminous coal mining. The volume of methane in the ventilation air of Poland's bituminous coal mines approached 870 m m^3 in 2006 [1]. For safety reasons, methane concentration in ventilation air does not exceed 0.75%, which means that methane is not utilized to its full extent, and 581m m^3 are released into the atmosphere [1]. Despite its low concentration in the atmosphere (1774 ppbv), methane is one of the greenhouse gases that have contributed to the recently observed distinct climate changes due to global warming. As a greenhouse gas, methane poses environmental hazards that are 25 times those from carbon dioxide [2]. Therefore methane must be removed from mine ventilation air.

The most suitable method for removing methane from ventilation air in coal mines is catalytic combustion. Methane is most efficiently combusted over palladium catalysts whose activity in this process is influenced by a diversity of factors such as the concentration and type of the Pd precursor chosen, the method used for catalyst preparation and pretreatment, and also the reaction conditions [3–9].

Because of the large volume of gases being combusted, it is advisable to use monolithic honeycomb catalysts when oxidizing ventilation air methane. The advantages of monolithic

catalysts are the following: low flow resistance of gases at high flow velocities, low pressure drop in gases flowing through the catalyst, good mass and heat transport, high thermal and chemical stability, high catalytic efficiency per unit mass of active phase [10, 11].

The objective of this work was to compare the activity of monolithic catalysts containing 5 g Pd in 1 dm^3 catalyst: a commercial catalyst purchased for this purpose and a catalyst manufactured using a preparation method developed at Wrocław University of Technology. Catalytic activity was tested in methane oxidation conducted in a prototype large laboratory installation at different methane concentrations in air and different air flow rates.

2. Methods of catalyst preparation and testing

The catalyst was supported on a metal monolith made of 0.05 mm thick heat-resisting FeCr20Al5 steel foil (Sandvik), rolled up to form a cylinder with a height of 150 mm and diameter of 100 mm. The support had a honeycomb cross-section. The active layer consisted of 5 g Pd in 1 dm^3 catalyst deposited by impregnation of the support (catalyst 1). The catalyst was calcined in air at 500ºC for 3 h. The commercial catalyst purchased for this study was of the same volume and had the same Pd content (catalyst 2).
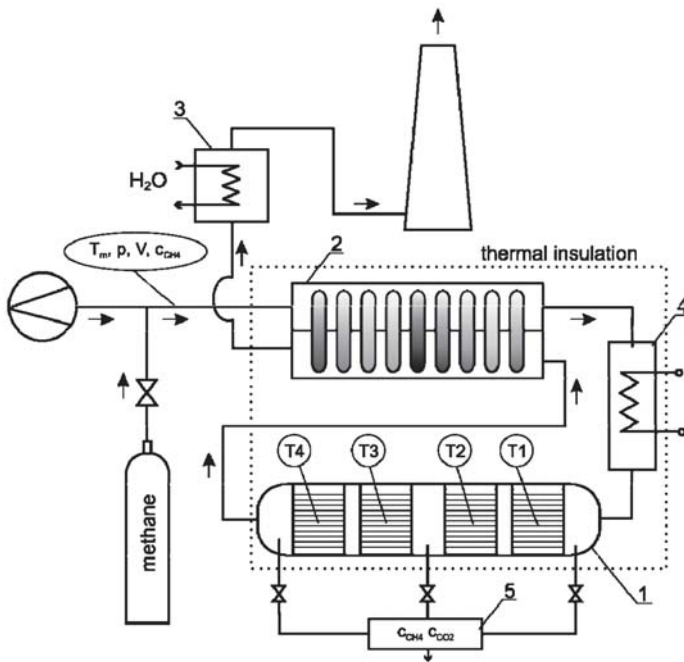

Fig. 1. Flow diagram of the large laboratory installation for methane oxidation:
1 — packed bed reactor, 2 — heat-pipe exchanger, 3 — water heat exchanger,
4 — heater, 5 — CH$_4$ & CO$_2$ analyzer

The activities of the catalysts were tested in the oxidation of 0.1–0.92% CH_4 in air. Air flow rates varied from 25 to 30 m^3/h. Catalytic activity tests consisted in methane oxidation over catalysts in oxidized form and were carried out in a large laboratory installation (Fig. 1). The progress of the methane oxidation process could be observed on a screen, which showed the flow diagram of the installation and actual process parameters. Inlet and outlet methane concentrations were measured with a Guardian PLUS (0–1% methane) or a Nanosens DP-27 (0–5% CH_4 and 0–5% CO_2) analyzer.

3. Results and discussion

The methane combustion activity of a bed of 4 monolithic 5 gPd/dm^3 catalysts manufactured at Wrocław University of Technology (catalyst 1) was compared with the activity of a bed comprising 4 commercial monolithic catalysts of the same volume and palladium content (catalyst 2). The methane oxidation process was carried out in a large laboratory system, and the catalyst beds were on stream for 60 h and 99 h, respectively.

The progress of oxidation of 0.5–0.92% methane in air over 2 and 4 monolithic catalysts 1 at air flow rates of 25 m^3/h and 30 m^3/h is visualized in figures 2 and 3, respectively. At the air flow rate of 25 m^3/h and CH_4 concentrations in air of 0.75% or 0.92%, methane was combusted with similar efficiency (Fig. 2). During catalytic oxidation of 0.5% methane in air the quantity of heat released was lower than during oxidation of 0.75–0.92% methane. This is why the decrease of methane concentration in air to 0.5% necessitated an increase in the temperature of the gas entering the catalyst, in order to prevent a decline in the temperature of the catalyst bed and, consequently, in the extent of methane conversion.
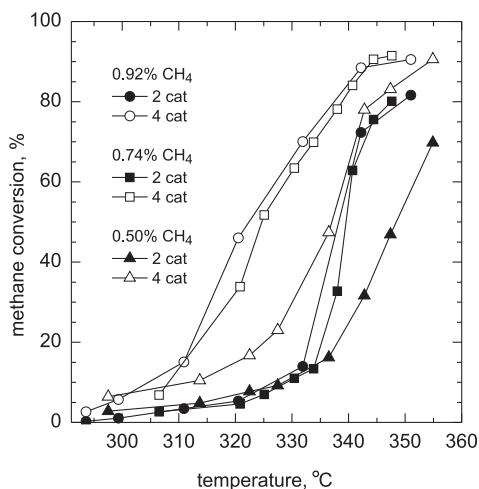

Fig. 2. Combustion of methane in air
over 2 and 4 monolithic 5 gPd/dm^3 catalysts (catalyst 1)
at different methane concentrations and an air flow rate of 25 m^3/h

In order to achieve 90% conversion of methane at the air flow rate of 25 m^3/h, it was necessary to heat the gas entering the catalyst bed to the temperature of 343–354°C. This temperature depended on methane concentration in air and increased with its decline.
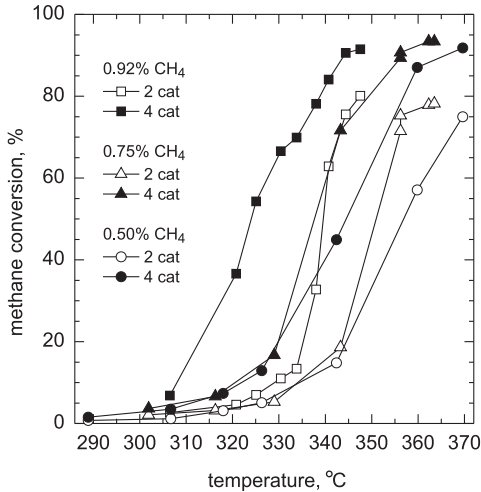

Fig. 3. Combustion of methane in air
over 2 and 4 monolithic 5 gPd/dm^3 catalysts (catalyst 1)
at different methane concentrations and an air flow rate of 30 m^3/h

Methane oxidation followed a similar pattern when air flow rate was increased to 30 m^3/h. Also in this case did the decline in methane concentration in the air from 0.75% to 0.5% necessitate a rise in the temperature of the gas entering the catalyst (Fig. 3). Methane oxidation over the four catalysts was satisfactory when conducted at the air flow rate of 30 m^3/h and methane concentration in air of 0.92%. In order to achieve 90% methane conversion, the gas entering the catalyst had to be heated to 344°C.

Over catalyst 2, at the air flow rate of 25 m^3/h, conversion increased with the increase of methane concentration in air. At concentrations of 0.1% and 0.2%, methane conversions were similar (Fig. 4 and 5). Since these concentration values are low, the plots that visualize temperature changes in particular catalysts in the bed display no significant rise in temperature caused by heat release in the reaction of methane oxidation, although the temperature of the gases entering the catalyst increase (Fig. 6a). At methane concentrations of 0.1% and 0.2%, gas temperature after the catalyst bed was only by 10°C higher than the temperature of the gas entering the catalyst. Under such conditions the installation could work only because the gas was heated by energy from outside (by heaters). When methane concentration in air was 0.8%, the temperature of the gases after the catalyst bed exceeded the temperature of the gas entering the catalyst by approximately 140°C (Fig. 6b). In this way a positive heat effect was achieved for the process.
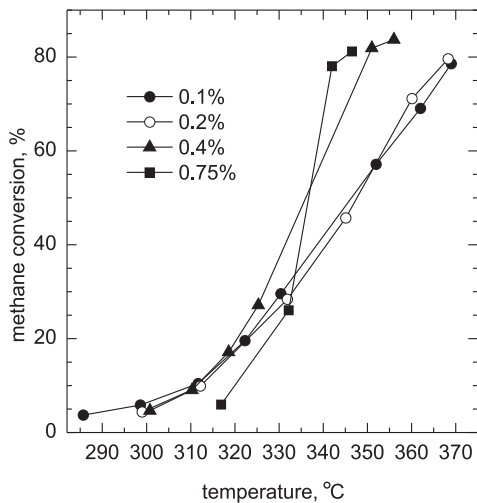
Fig. 4. Combustion of methane in air
over 2 monolithic 5 g Pd/dm^3 catalysts (catalyst 2)
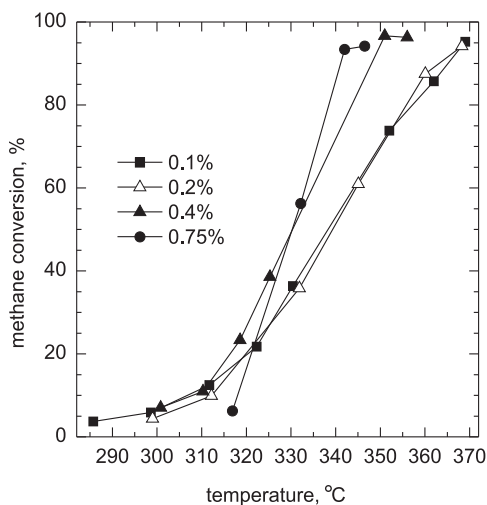at different methane concentrations and an air flow rate of 25 m^3/h

Fig. 5. Combustion of methane in air
over 4 monolithic 5 g Pd/dm^3 catalysts (catalyst 2)
at different methane concentrations and an air flow rate of 25 m^3/h

The plots in Figures 4 and 5 show that with any of the CH$_4$ concentrations in air, approximately 80% of methane was converted over the first two monoliths in the bed, the remainder being combusted over monoliths 3 and 4.
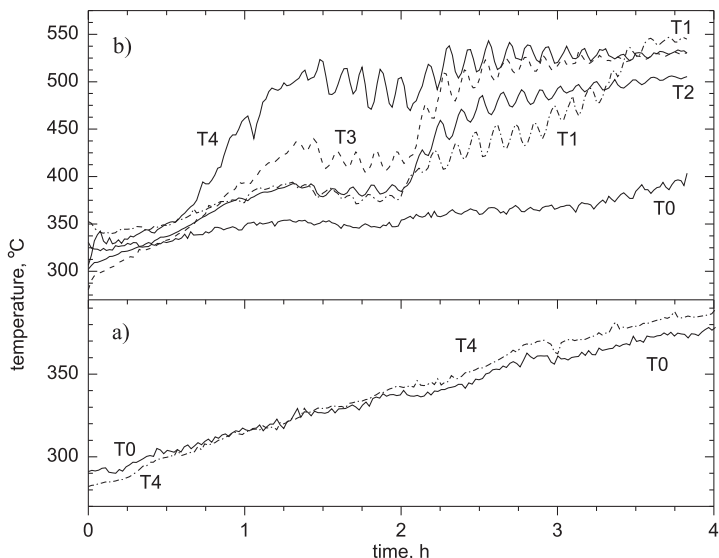
Fig. 6. Temperature distribution in the catalytic bed (catalyst 2) at methane concentrations in air of 0.1%: a) and 0.8%; b) and air flow rate of 25 m³/h. $T0$ — gas temperature before the catalyst, $T1$, $T2$, $T3$, $T4$ — temperatures after catalysts 1, 2, 3, 4, respectively

For catalyst 2, at the air flow rate of 30 m³/h, conversion increased when methane concentration in air rose from 0.4% to 0.75%. At concentrations of 0.4% and 0.52%, methane conversions were comparable.
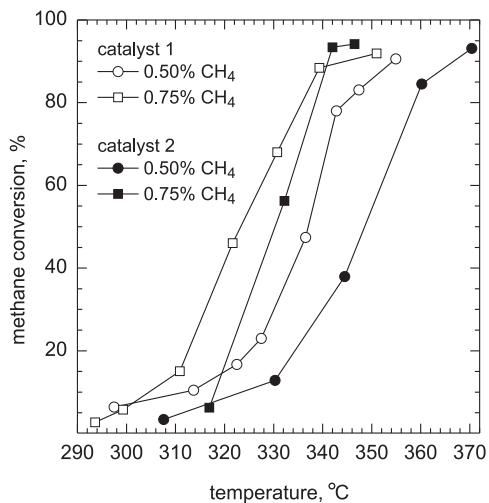

Fig. 7. Comparison of methane conversion over 4 monolithic 5 gPd/dm³ catalysts (catalysts 1 and 2). Methane concentration, 0.5% and 0.75%; air flow rate, 25 m³/h
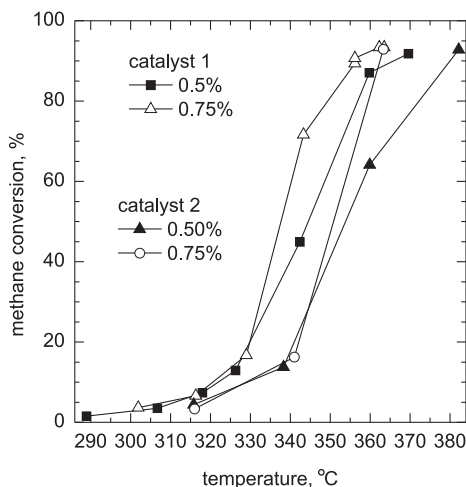
Fig. 8. Comparison of methane conversion
over 4 monolithic 5 gPd/dm^3 catalysts (catalysts 1 and 2).
Methane concentration, 0.5% and 0.75%; air flow rate, 30 m^3/h

At the air flow rate of 25 m^3/h, 90% conversion of methane was achieved when gas mixture temperatures before the catalyst bed ranged from 342 to 365ºC for catalyst 2, and from 343 to 354ºC for catalyst 1, depending on methane concentration in air. At the air flow rate of 30 m^3/h, the temperatures required for achieving 90% conversion varied from 363 to 380ºC and from 355 to 362ºC for catalyst 2 and catalyst 1, respectively, and increased when methane concentration in air declined from 0.75 to 0.52%.

Figures 7 and 8 enable comparison of methane conversion over beds of 4 monolithic catalysts manufactured at Wrocław University of Technology and over 4 commercial catalysts with the same Pd content of 5g/dm^3. At both air flow rates, 25 m^3/h and 30 m^3/h, and methane concentrations in air of 0.5% and 0.75%, the catalyst manufactured at Wrocław University of Technology exhibited a higher activity for methane oxidation.

4. Conclusions

The monolithic palladium catalyst manufactured according to the preparation method developed at Wrocław University of Technology shows a higher methane oxidation activity than does the commercial catalyst with the same palladium content.

Methane conversion over 4 monolithic 5 gPd/dm^3 catalysts (catalysts 1 and 2) declines when air flow rate rises from 25 dm^3/h to 30 m^3/h and increases with the increase of methane concentration in air from 0.5% to 0.92%.

The bed of 4 monolithic catalysts designed at Wrocław University of Technology performs best at the air flow rate of 25 m^3/h and methane concentration in air from 0.75 to 0.92%.

Under such conditions, the temperature of the gas entering the catalyst should be close to 343ºC.

The monolithic 5 gPd/dm^3 catalysts examined display a high methane oxidation activity, which makes them applicable to the removal of methane from coal mine ventilation air.

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