

Activity of monolithic Pd/Al₂O₃ catalysts in the combustion of mine ventilation air methane

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The activity of Pd/Al₂O₃ catalysts increases when Pd content is increased from 1% to 2%. Among these catalysts, 2%Pd/Al₂O₃ shows the highest methane combustion activity. In a reduced form, the catalyst displays a higher activity than in the oxidized form. 24-hour ageing at 600°C to 800°C lowers the catalytic activity of 2%Pd/Al₂O₃ due to Pd crystallite sintering. After 110-hour oxidation of 1% methane in air over 2%Pd/Al₂O₃, conversion decreases from 100% to 88%. Upon reduction with hydrogen (performed after 24-hour ageing at 700°C and 110-hour methane oxidation), the 2%Pd/Al₂O₃ catalyst regains its initial activity. The high activity of Pd catalysts renders them suitable for methane removal from coal mine ventilation air at high gas flow velocities and temperatures lower than 600°C.

Keywords: catalytic oxidation of methane, monolithic catalysts, mine ventilation air.

INTRODUCTION

Methane emissions come from a variety of sources, such as gas transport systems, crude oil and earth gas refining installations, agriculture, industry, waste processing sectors, or bituminous coal beds. In the time span of 1990–2005 a continuing rise was observed in the amount of methane emitted into the atmosphere. Atmospheric methane concentrations have increased from 715 ppbv in the pre-industrial epoch to 1778 ppbv in recent times¹. It is estimated that by the year 2020 methane emission will have increased by about 12 to 16% in such sectors as coal mining and agriculture². Despite its low concentration, methane ranks second among the most important anthropogenic greenhouse gases that have contributed to the recently observed distinct climate changes due to global warming. Taking into account the short lifetime of atmospheric methane, and making use of the Global Warming Potential as a basis for CO₂ equivalence, methane as a greenhouse gas is 25 times as hazardous as carbon dioxide on a per unit mass basis¹.

The emission of methane (which, for safety, must be removed from the mine's ventilation air) is an inherent part of bituminous coal mining. The annual volume of methane entering the atmosphere with ventilation air of Poland's bituminous coal mines³ approaches 581m m³. Methane concentration in ventilation air does not exceed 0.75%. In spite of its low concentration, ventilation air methane from coal mines may be used as a fuel in combustion processes, as well as in thermal and catalytic reverse flow reactors, catalytic-monolith combustors, catalytic lean burn gas turbines, recuperative gas turbines, or concentrators².

The most effective method for removing methane from the ventilation air in coal mines is catalytic combustion, and Pd catalysts display a high activity in this process^{4–12}. The Pd precursors most frequently used are Pd(NO₃)₂, PdCl₂, H₂PdCl₄^{4–7}, as well as organic Pd salts dissolved in diverse solvents^{6,7}. The type of the precursor used influences the dispersion of Pd and the form in which Pd occurs on the surface of the Pd/Al₂O₃ catalyst⁷. There is no agreement about the optimal Pd content of the catalyst, and it still remains unclear whether PdO,

metallic Pd, or the mixed phase Pd/PdO_x is the active form of palladium in methane oxidation^{4,5}. The optimal Pd content for the Al₂O₃ support varies from 0.5% to 2%; higher Pd content lowers specific activity. Escandon *et al.* express the opinion that reduction does not change the methane oxidation activity of the Pd/Al₂O₃ catalyst⁸. Choudhary *et al.* have found that with the same Pd content, the catalyst obtained by partial oxidation of Pd⁰/Al₂O₃ shows much better properties in methane oxidation (regardless of the temperature applied) than the catalyst obtained by partial reduction of PdO/Al₂O₃⁹.

Because of the large volume of the gases being combusted, it is advisable to use monolithic honeycomb catalysts when oxidizing methane in mine ventilation air. The benefits are manifold: low flow resistance of gases at high flow velocities (>105h⁻¹), low pressure drop in gases flowing through the catalyst, good mass and heat transport, high catalytic efficiency per unit mass of active phase, easy separation, as well as high thermal and chemical stability of the catalyst¹⁰.

The aim of this work was to examine the activity and potential use of Pd-based monolithic catalysts supported on heat-resisting foils (FeCrAl) for the combustion of ventilation air methane in coal mines. Consideration was given to the following issues: the effect of Pd load and dispersion on the methane combustion activity of Pd catalysts, and the effect of elevated temperature and reduction with hydrogen on the activity and stability of the monolithic 2%Pd/Al₂O₃ catalyst during methane combustion.

EXPERIMENTAL

The catalysts examined were supported on metal monoliths made of a 0.05 mm thick heat-resisting FeCr20Al5 steel foil (Sandvik), rolled up to form a cylinder, which was 70 mm high, 26 mm in diameter, and had a honeycomb cross-section (112 triangular channels/cm² support). Since the structure of the support was a nonporous one, its roughness was increased by etching in 10% sulphuric acid at 60°C for 2 min. The surface of the support was washcoated with Al₂O₃ by the sol-gel method, and then calcined at 400°C in air for 3 h. The washcoat accounted for 4.5 wt. % of the support mass. The active layer

consisted of Pd deposited by impregnating the support with a $\text{Pd}(\text{NO}_3)_2$ and 0.15% $\text{Al}(\text{OH})_3$ sol solution. The Pd content of the catalysts ranged from 0.5 to 2% of the support mass. The catalysts were calcined at 500°C in air for 3 h. The 2%Pd/ Al_2O_3 catalyst was aged in air at 600°C, 700°C and 800°C for 24 h.

X-ray measurements were performed using a PANalytical X'Pert Pro diffractometer with a Cu radiation source $K\alpha$ of a wavelength $\alpha = 1.5418 \text{ \AA}$.

Active metal surface area and dispersion of Pd were calculated in terms of hydrogen chemisorption at 110°C, using an ASAP 2010C apparatus (Micromeritics, USA). The same apparatus was used to examine the specific surface area (BET) of Al_2O_3 .

Pd particle size was determined by Transmission Electron Microscopy (TEM), using Philips CM20 (200kV) TWIN. Catalyst surfaces were examined by scanning electron microscopy (SEM), using a Nova NanoSEM 230 microscope (FEI). Sample composition was established by energy dispersive X-ray spectrometry (EDXS), using an EDAX Pegasus XM4 spectrometer (with an SDD Apollo 40 detector).

To determine the adhesion of the active layer to the support during temperature variations, the catalyst samples were passed through 4500 cycles of heating to 1000°C for 5 s and cooling to room temperature for 10 s. Heat resistance was expressed as the relative change in the mass of the catalysts, calculated as the ratio of the mass change in the catalyst after a certain number of cycles to the initial total mass of the catalyst.

Catalytic activity was tested in the oxidation of 1% or 0.5% CH_4 in air. Use was made of a flow reactor placed in a heater with a programmed temperature increment (heating ramp 3°C/min), gas hourly space velocity (GHSV) being set to 5800 h^{-1} on the total monolith volume. The temperature of the catalysts was measured with a K-type thermocouple in the canal of the monolith, at a depth of 16 mm from the gas outlet. Catalytic activity tests consisted of methane oxidation

over catalysts in the oxidized form and catalysts reduced with hydrogen at 200°C for 1 h. The effect of GHSV on methane conversion was examined over the range of 4500–7000 h^{-1} . Inlet and outlet CH_4 concentrations were measured with a Nanosens DP-27 analyzer. The accuracy of the analyzers used in this study was $\pm 5\%$ of the measured value.

RESULTS AND DISCUSSION

To increase its specific surface area, the nonporous monolithic metal support was covered with an Al_2O_3 washcoat, which had a specific surface area of 335.1 m^2/g and a pore diameter of 4.98 nm. The dispersion of palladium on the alumina washcoat is influenced by the Pd content of the catalyst. Thus, when Pd content increased from 0.5% to 2%, Pd dispersion decreased from 14% to 2.4%, and Pd crystallite size increased from 0.8 nm to 46 nm (Table 1).

XRD spectra of fresh Pd/ Al_2O_3 catalysts in the oxidized form (with Pd contents of 1 to 2%) exhibit a PdO peak at $2\theta = 34^\circ$, as well as peaks of heat-resisting FeCr20Al5 steel.

Methane combustion activity of the monolithic Pd catalysts was found to improve when Pd content increased from 1% to 2% (Fig. 1a). It was also observed that when Pd content ranged between 0.5 and 1.5%, the effect of Pd dispersion on the catalytic activity was stronger than the effect of Pd content. This manifested in the higher

Table 1. Dispersion, specific surface area and crystallite size of palladium

Catalyst	Dispersion of Pd [%]	Specific surface area of Pd [m^2/g sample]	Average size of Pd crystallites [nm]
2%Pd/ Al_2O_3	2.4	0.21	46
1.5%Pd/ Al_2O_3	2.8	0.19	39
1%Pd/ Al_2O_3	4.4	0.22	23
0.5%Pd/ Al_2O_3	14.0	0.16	0.8

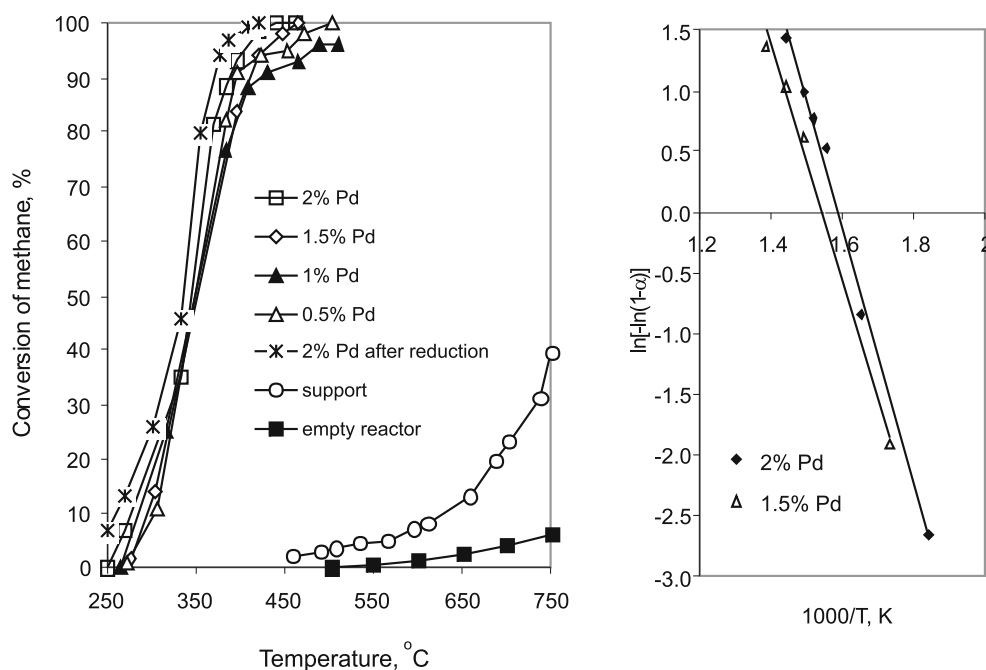


Figure 1. Methane conversion as a function of temperature for $x\%\text{Pd}/\text{Al}_2\text{O}_3$ ($x=0.5-2$) catalysts in oxidized form, as well as the activity of 2%Pd/ Al_2O_3 catalyst upon hydrogen reduction (a), Arrhenius plots (b)

activity of the 0.5%Pd/Al₂O₃ catalyst (Pd dispersion of 14%) as compared to the 1%Pd/Al₂O₃ catalyst (Pd dispersion of 2.8%), or (at temperatures lower than 420°C) to the catalyst with the 1.5% Pd content (Pd dispersion of 4.4%). However, the 2%Pd/Al₂O₃ catalyst exhibited the highest activity, in spite of a low Pd dispersion (2.4%). Subjected to 1-hour reduction with hydrogen at 200°C, the catalyst displayed a higher activity for methane oxidation than it was in the oxidized form (Fig. 1a). According to Ferrauto¹¹, palladium supported on Al₂O₃ occurs in the form of PdO when it is heated in air at a temperature lower than 750°C. The reduction of PdO begins at 750°C and progresses gradually; at 850°C, only metallic Pd is present on the catalyst surface. Within the temperature range of 250–550°C, over which methane combustion was conducted in our study, oxidation of superficial Pd⁰ seemingly occurred after catalyst reduction. On the catalyst surface appeared a mixed phase, PdO_x/Pd⁰, which was more active than PdO^{11,12}. Owing to the presence of PdO_x/Pd⁰, the 2%Pd/Al₂O₃ catalyst showed a higher activity upon reduction than it did in the oxidized form, when the presence of PdO was detected (XRD).

No homogeneous reactions were found to occur at temperatures lower than 500°C, at which methane was oxidized over the catalysts tested. Experiments with CH₄ oxidation in an empty reactor show that a homogeneous reaction initiates at temperatures higher than 600°C; at 750°C, however, only 6.2% of CH₄ is converted. Over a catalyst with an Al₂O₃-washcoated support, a homogeneous reaction sets on at temperatures higher than 530°C, and methane conversion at 750°C totals 39.4% (Fig. 1a).

Figure 1b presents the activity data (Arrhenius coordinates) recorded during CH₄ combustion over x%Pd/Al₂O₃ catalysts. These data were determined from the experimental conversion by assuming that the reaction runs in an isothermal ideal plug-flow reactor and is first order with respect to methane and zero order with respect to oxygen concentration. For the catalysts 1.5%Pd/Al₂O₃ and 2%Pd/Al₂O₃, these assumptions well describe the experimental data up to the temperature of 420°C (98% conversion of methane) (Fig. 1b). The apparent activation energies determined for these catalysts are 85.4 kJ/mol and 87.6 kJ/mol (R²=0.99), respectively. They are in good agreement with those ranging between 70 and 90 kJ/mol, reported previously in the literature^{5,13–15}. For the 1%Pd or 0.5% Pd catalyst, over which methane oxidation occurs at higher temperatures, a deviation of the Arrhenius plot from linearity is observed, and the curvature of the line appears at 400°C. This indicates that at a high temperature, in the presence of these catalysts, the reaction is limited by the rate of mass transport to the surface.

The combustion of mine ventilation air methane is an exothermic process, and thus leads to a significant rise in the temperature of the catalyst bed in the reactor. If no cooling is applied, this may cause the temperature of the catalyst bed to exceed 500°C, at which the monolithic Pd/Al₂O₃ catalysts were calcined. To determine its heat resistance, the 2%Pd/Al₂O₃ catalyst was subjected to ageing at 600–800°C for 24 h. After 24-hour ageing at 600°C, the activity of 2%Pd/Al₂O₃ decreased, and in consequence 99% conversion of CH₄ was achieved at 527°C, while over a fresh catalyst 100% conversion was

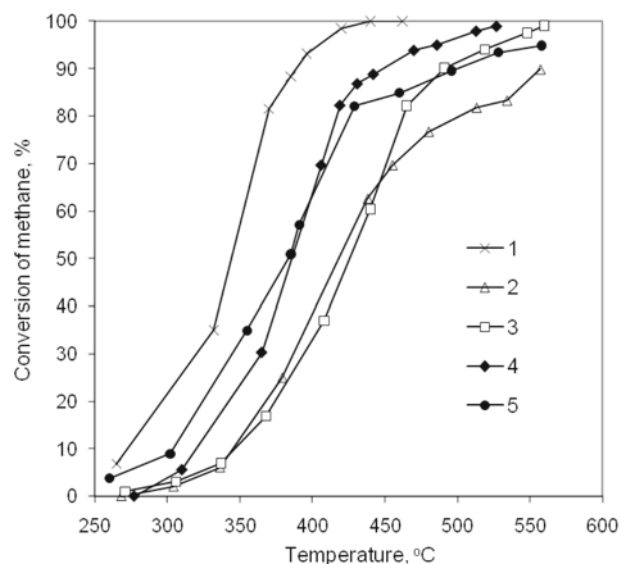


Figure 2. Activity of fresh 2%Pd/Al₂O₃ (1), after ageing at 800°C (2), 700°C (3), and 600°C (4), as well as after ageing at 700°C and reduction with hydrogen (5)

reached at 440°C (Fig. 2). When ageing temperature was increased to 700°C and 800°C, this was concomitant with a further decrease in catalytic activity during methane oxidation (Fig. 2). Thus, with the ageing temperature of 700°C, methane conversion at 560°C totalled 99%, and decreased to 90% when ageing temperature was increased to 800°C. For the 2%Pd/Al₂O₃ catalyst, the temperatures from 700°C to 800°C are within the range where palladium undergoes sintering. Pd crystallites on the surface of fresh 2%Pd/Al₂O₃ (calcined at 500°C for 3 h) are very small. As a consequence, they cannot be seen in the SEM micrograph (Fig. 3a), but they are visible in the TEM pattern (Fig. 4). SEM micrographs demonstrate that the rise in ageing temperature to 800°C is paralleled by the appearance of white crystallites containing large amounts of palladium (Fig. 5). EDXS has shown that the white crystallite marked on the catalyst surface (Fig. 5) consists of 38.95 At% of palladium, 57.49 At% of oxygen and 3.56 At% of aluminium. Thus, the crystallites are composed mainly of PdO and contain a small amount of Al₂O₃. The increase in the quantity and size of the crystallites with ageing temperature substantiates the sintering of PdO, which reduces the activity of the 2%Pd/Al₂O₃ catalyst. Ageing at 700°C for 24 h, followed by reduction with hydrogen at 200°C for 1 h, noticeably increased methane oxidation activity at temperatures lower than 430°C. With the rise in temperature to approximately 500°C, the activity of the catalyst after ageing equalled the activity of the catalyst after ageing and reduction (Fig. 2). This implies that while the catalyst is exposed to the air stream, palladium re-oxidizes gradually, and thus reduces catalytic activity. As reported in the literature^{4,5}, Pd⁰ shows a lower activity for methane oxidation than PdO does, since not only the oxygen from its gaseous phase, but also the oxygen from the crystalline lattice of PdO participates in the oxidation reaction. However, in the course of the reaction, the Pd⁰ that formed on the catalyst surface upon reduction becomes covered by an oxygen layer and soon re-oxidizes to PdO. Activation pre-treatment (oxidation or reduction) of Pd/ZrO₂ affects the redox behaviour of the

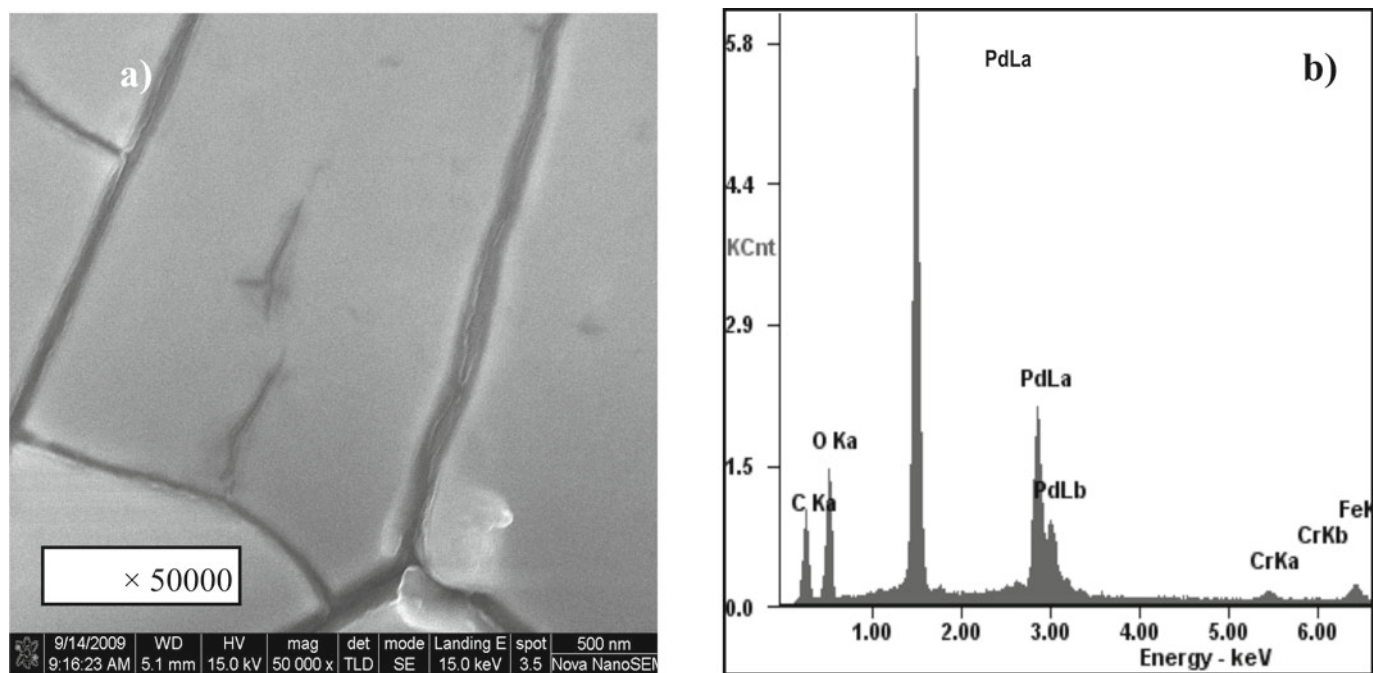


Figure 3. SEM micrograph (a) and X-ray microanalysis (b) of the surface of fresh 2%Pd/Al₂O₃ catalyst

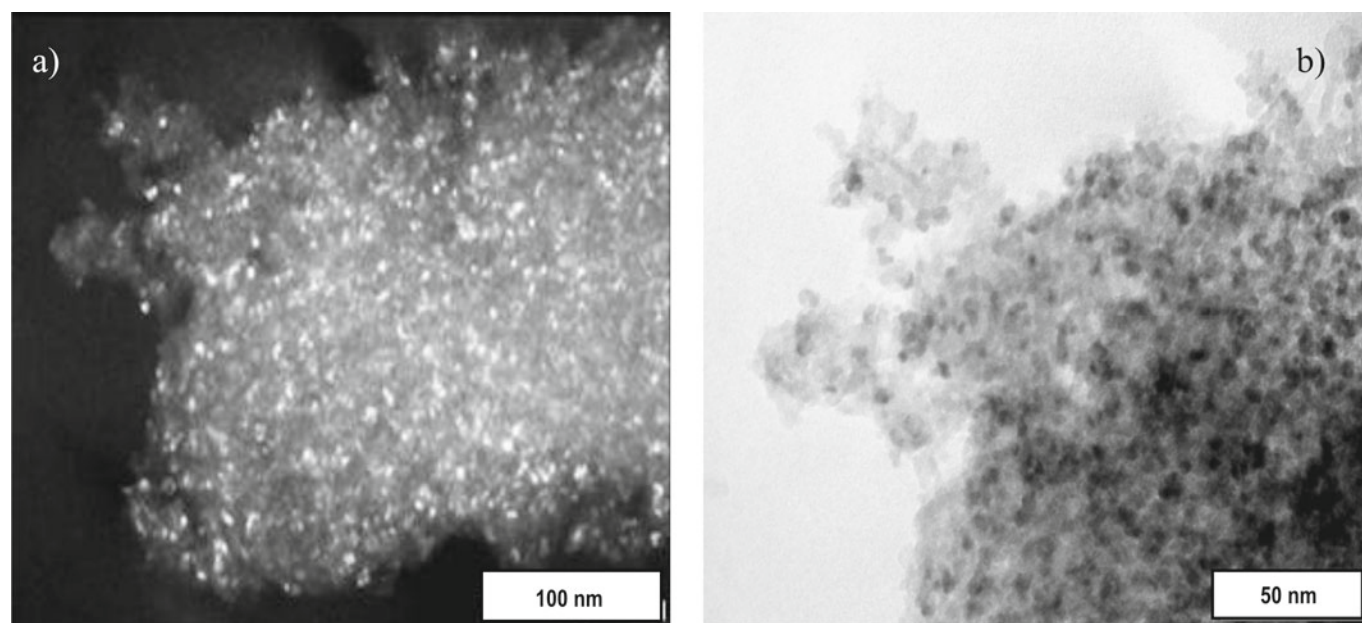


Figure 4. Dark-field TEM (a) and HRTEM (b) micrographs of fresh 2%Pd/Al₂O₃ catalyst

catalyst. Subjected to pre-reduction at low temperature and, again, to oxidation, palladium catalysts (even those with large crystallites) show a higher activity than do unreduced catalysts^{5,9,16}. This is attributable to a larger content of PdO which readily undergoes reduction at lower temperatures.

The monolithic catalysts under study were tested for the adhesion of the active layers to the supports under the conditions of alternate cycles of heating to 1000°C and subsequent cooling to room temperature. Differing in their thermal expansion, the active layers suffer cracking that may lead to their fall-off, and thus reduce catalytic activity. After 4500 cycles of heating and cooling, the relative mass changes amount to +0.43% (1.5%Pd/Al₂O₃) and +1.02% (2%Pd/Al₂O₃) (Fig. 8). No reduction in the sample mass was observed in the course of the study, which indicates that the active layer adheres to the support very well. The increase in the sample mass – which is the greater, the higher the Pd content

of the catalyst is – implies that during cooling of the catalysts to room temperature the bulk of palladium was oxidized to PdO.

The most active catalyst, 2%Pd/Al₂O₃, was chosen for 1% atmospheric CH₄ oxidation, which was conducted at 420°C for 110 h. After 110 h on stream, methane conversion dropped from 100% to approximately 88%. Reduction with hydrogen (performed at 200°C for 1 h after 110 hours on stream) enhanced methane oxidation activity: at temperatures higher than 380°C, the catalyst in reduced form was as active as in the fresh state. At lower temperatures, CH₄ conversion was slightly higher over the fresh catalyst (Fig. 6).

During combustion of ventilation air methane, a large gas volume where methane concentration accounts for less than 0.75% passes through the catalyst. During the oxidation of 0.5% methane in air over the 2%Pd/Al₂O₃ catalyst, the increase in GHSV from 4500 h⁻¹ to 5800 h⁻¹ noticeably reduced methane conversion. Further increase

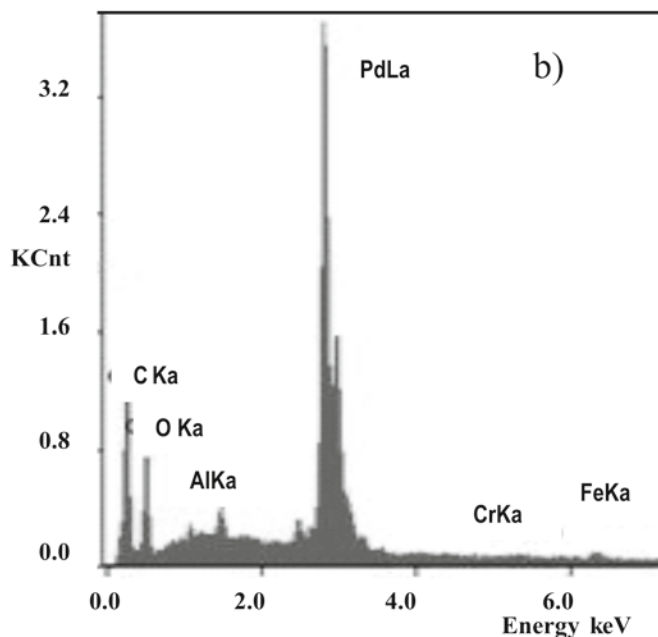
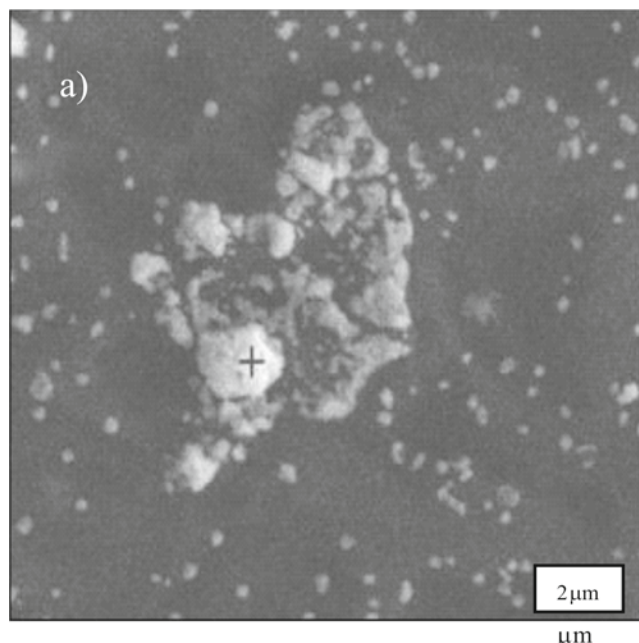


Figure 5. SEM micrograph of 2%Pd/Al₂O₃ catalyst after ageing at 800°C (a) and X-ray microanalysis at the marked point on the catalyst's surface (b)

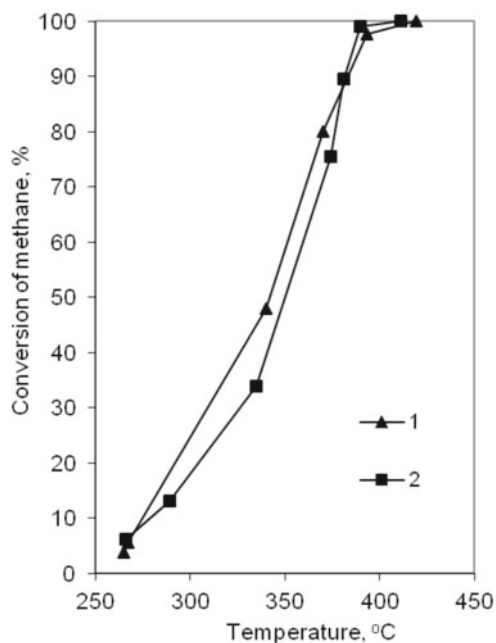


Figure 6. Activity of fresh 2%Pd/Al₂O₃ (1) and 2%Pd/Al₂O₃ reduced with hydrogen after 110 h of methane oxidation (2)

in GHSV to 7000 h⁻¹ changed methane conversion only slightly. With GHSV of 4500 h⁻¹, 100% conversion of CH₄ was obtained at 438°C, whereas with GHSV of 5800 h⁻¹ or 7000 h⁻¹ at about 450°C (Fig. 7).

CONCLUSIONS

Methane combustion activity of palladium catalysts increases with the increase in Pd content from 1 wt.% to 2 wt.%. Reduction with hydrogen at 200°C enhances the activity of the 2%Pd/Al₂O₃ catalyst.

Ageing over the temperature range of 600°C to 800°C for 24 h lowers the activity of the 2%Pd/Al₂O₃ catalyst due to the sintering of Pd crystallites. Reduction with hydrogen at 200°C after ageing at 700°C for 24 h increases its activity.

After 110-hour oxidation of 1% methane in air at

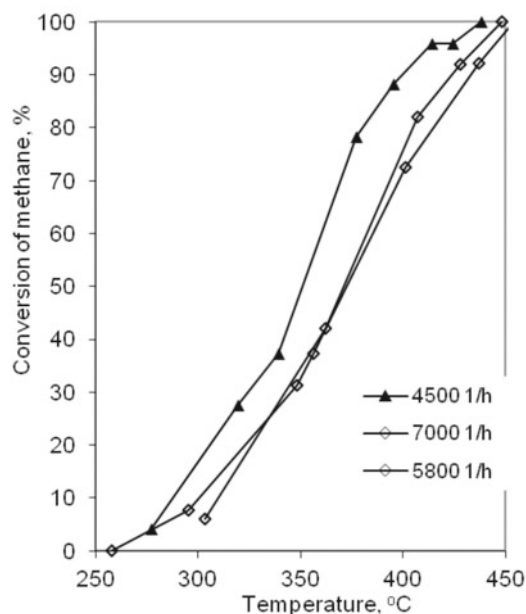


Figure 7. Effect of GHSV on methane conversion over 2%Pd/Al₂O₃ during oxidation of 0.5% CH₄ in air

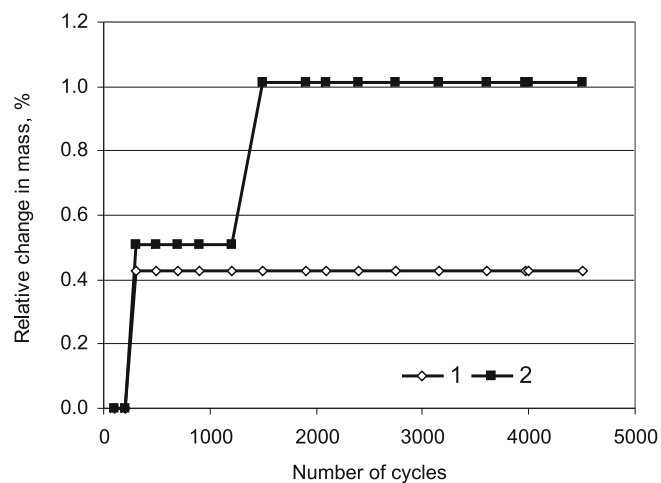


Figure 8. Heat resistance of Pd/Al₂O₃ catalysts: 1.5%Pd/Al₂O₃ (1); 2%Pd/Al₂O₃ (2)

420°C over the 2%Pd/Al₂O₃ catalyst, conversion falls from 100% to 88%. Upon reduction with hydrogen after 110 h on stream, the catalyst regains its initial activity.

Palladium catalysts display a high methane oxidation activity, which renders them applicable to the removal of methane from coal mine ventilation air at a high GHSV and temperatures lower than 600°C.

ACKNOWLEDGEMENT

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