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EFFECT OF PROMOTOR TYPE AND REDUCER ADDITION ON THE ACTIVITY OF PALLADIUM CATALYSTS IN OXIDATION OF METHANE IN MINE VENTILATION AIR

The aim of the study was to examine how the palladium precursors such as $Pd(NO_3)_2$ or $PdCl_2$ and the reducers added (hydrazine hydrate or EDTA) influence methane combustion activity of monolithic palladium catalysts. Palladium nitrate was found to be a better Pd precursor, and the catalysts obtained displayed a noticeably higher activity in methane oxidation. The addition of hydrazine hydrate to 1% Pd/Al_2O_3 catalyst increased its activity when $PdCl_2$ was used as the palladium precursor. With $Pd(NO_3)_2$ as the palladium precursor, the addition of reducers – hydrazine hydrate or EDTA – decreased the activity of the monolithic palladium catalysts tested.

1. INTRODUCTION

Palladium-based catalysts are characterized by a high methane combustion activity which is influenced by the Pd precursor, the method of catalyst preparation and pretreatment, as well as the reaction conditions applied [1–7]. Pd precursors most frequently used are $Pd(NO_3)_2$, $PdCl_2$ or H_2PdCl_4 [1–6], but use can also be made of palladium acetate, palladium propionate or other organic palladium salts dissolved in a variety of solvents [3, 4]. Catalysts obtained by dissolving those salts in carboxylic acids (acetic and propionic) exhibit very high activity [3]. The type of the precursor used influences the dispersion of Pd and the form in which it occurs on the surface of the Pd/Al_2O_3 catalyst [4]. When palladium acetate dissolved in toluene is used as a Pd precursor, the extent of Pd dispersion is higher than when use is made of $Pd(NO_3)_2$ or H_2PdCl_4. It was reported that Pd dispersion did not change after 24 h ageing of the Pd/Al_2O_3 catalyst at 650 °C [4]. Pd particles of the size smaller than 5 nm were

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quickly oxidized to PdO which alone was present on the catalyst surface. When Pd particles were of a larger size than 15 nm, palladium occurred in a metallic form and was covered with a PdO layer [4]. The form of Pd occurrence during methane oxidation – Pd^0, PdO or PdO_x/Pd – is ambiguous [1–4]. Depending on the reaction conditions (partial pressure of oxygen, temperature, composition of reaction mixture), PdO may undergo reduction or re-oxidation. The hydrocarbons present in the gas may induce the reduction of PdO at temperatures substantially lower than the temperature of its thermal decomposition in air or inert gas [6].

Methane emission is an inherent part of hard coal mining. As the emitted volume is large, methane has to be removed from the pit shaft with ventilation air for safety reasons. As methane concentration in ventilation air is low, not exceeding 0.75%, it cannot be fully utilized and in most instances methane is released into the atmosphere. The annual volume of methane entering the atmosphere with ventilation air approaches 581 million cubic meters [8]. Methane is a greenhouse gas [9] with an environmental impact 23 times as strong as that of carbon dioxide, and its presence in the atmosphere contributes to climatic changes and consequently to global warming.

Continual increase in the concentration of air-borne CH_4 necessitates its removal from mine ventilation air. The best method for its removing in coal mines is catalytic combustion. Palladium catalysts on monolithic supports show a high activity in this process. The supports that may be used in catalytic combustion are either ceramic monoliths fabricated from aluminium oxide, silica, cordierite or mullite, or metallic monoliths made from heat-resisting foil of a 0.04–0.05 mm thick. Each of them has to be washcoated, e.g. with γ-Al_2O_3 of a high specific surface area. The washcoat is added to increase the specific surface area of the metallic support and stabilize its surface so as to prevent crystallite growth (at high temperatures, the crystallites of active components undergo sintering, causing them to increase in size) [10]. The benefits of applying monolithic supports are manifold: low cost of the support, possibility of using a comparatively small amount of active layer, low flow resistance of gases at high flow velocities ($>10^5$ h^{-1}), which enables application of high gas hourly space velocities (GHSV) without considerable pressure drop on the catalytic layer [10]. As compared to ceramic monoliths, the walls of the support in metallic monoliths provide the catalyst with a larger free cross-section. As a result, the same conversion can be obtained at the volume of metallic monoliths which is by 20–30% lower than the volume of ceramic monoliths [10]. This is of importance when methane has to be removed from the ventilation air in coal mines because in that particular case large volumes of air are to be combusted, where methane concentration does not exceed 0.75%.

The aim of this work was to investigate the effect of Pd precursors and reducing agents chosen on the activity of the monolithic Pd catalyst in methane oxidation. The study included investigations into the specific surface area of the washcoat, Pd dispersion and size of Pd crystallites, as well as XRD and SEM examinations of catalyst surfaces.

2. METHODS OF PREPARATION AND INVESTIGATION OF THE CATALYST

The supports for the catalysts were metal monoliths made of a 0.05 mm thick, Al_2O_3 washcoated heat-resisting FeCr20Al5 steel foil. They were shaped into cylinders with the height and diameter of 70 mm and 26 mm, respectively, possessing a honeycomb cross-section with 112 triangular channels/cm^2 support. The washcoated support was calcined at 400 °C in air for 3 h. To obtain the active layer, 1% or 1.5% Pd (with the addition of 0.15% Al(OH)$_3$ sol solution) was deposited onto the support by impregnation. Palladium nitrate with Pd concentration of 19.69% or palladium chloride with Pd concentration of 20.04% was used as the palladium precursor. The catalysts were calcined at 500 °C in air for 3 h. To increase Pd dispersion, additional catalysts were prepared, where the washcoated monolithic support was impregnated with the solutions of two reducing agents: hydrazine hydrate or ethylenediaminetetraacetic acid (EDTA). As for hydrazine hydrate, the washcoated support was subject to 12 h drying at 105 °C, followed by 10 min impregnation with hydrazine hydrate solution at 50 °C. EDTA was deposited by impregnation of the support with 0.1 M EDTA solution at 70 °C for 30 min, or for 5 min (Pd(NO$_3$)$_2$) and 12 min (PdCl$_2$). Then the supports were subject to drying at 105 °C for 3 h, followed by deposition of 1.5% Pd from palladium nitrate or 1% Pd from palladium chloride. The catalysts are characterized in Table 1.

Table 1

Preparation conditions, Pd dispersion, and average size of Pd crystallites

Catalyst Pd/Al$_2$O$_3$ [%]	Pd precursor	Reducer added	Impregnation temperature and time	Pd dispersion [%]	Average size of Pd crystallites [nm]
1.5	Pd(NO$_3$)$_2$	no reducer	–	2.82	42
1.0	Pd(NO$_3$)$_2$	no reducer	–	4.43	33
1.5	Pd(NO$_3$)$_2$	0.1M EDTA	70 °C, 5 min	–	–
1.5	Pd(NO$_3$)$_2$	0.1M EDTA	70 °C, 30 min	0.83	133
1.5	Pd(NO$_3$)$_2$	hydrazine hydrate	50 °C, 10 min	1.79	62
1.0	PdCl$_2$	no reducer	–	–	61
1.0	PdCl$_2$	0.1M EDTA	70 °C, 12 min	–	–
1.0	PdCl$_2$	hydrazine hydrate	50 °C, 10 min	–	–

Methane combustion efficiency was tested using a laboratory flow reactor placed in a heater with a programmed temperature increment (heating ramp 3 °C/min). Over the catalysts, 1% methane in air was oxidized at GHSV of 5800 h^{-1}. Methane concentration in the gas mixture was measured with a Nanosens DP-27 analyzer.

BET surface area (S_{BET}), average pore size and pore volume of the washcoat were determined by nitrogen sorption at the temperature of liquid nitrogen, using the ASAP 2010C apparatus (Micromeritics, USA). Active surface and dispersion of Pd were

determined with the same apparatus, based on measurements of hydrogen chemisorption at 100 °C over the pressure range of 120–250 mm Hg.

XRD measurements were carried out using a PANalytical X'Pert Pro diffractometer with a Cu radiation source K_α of the wavelength of $\lambda = 1.5418$ Å. Use was made of the Bragg–Brentano scattering geometry. Morphology of the samples was examined by the scanning electron microscopy (SEM) with a Nova NanoSEM 230 microscope (made by FEI). Sample composition was determined by the energy dispersive X-ray spectrometry (EDXS), using an EDAX Pegasus XM4 spectrometer (with an SDD Apollo 40 detector) at 20 keV.

3. RESULTS AND DISCUSSION

Monolithic supports were covered with an Al_2O_3-based washcoat of the specific surface area (S_{BET}) of 335.1 m^2/g, total pore volume of 0.42 cm^3/g, and pore diameter of 4.98 nm. Pd dispersion in the monolithic catalysts was poor (Table 1). In the case of the 1.5% Pd/Al$_2$O$_3$ catalyst, impregnation of the washcoated support with EDTA or hydrazine hydrate solutions caused a decrease in Pd dispersion and consequently Pd crystallite growth. After 30 min of impregnation with EDTA, Pd dispersion dropped from 2.82% to 0.83%, and after 10 min of impregnation with hydrazine hydrate to 1.79%.

Impregnation of the support of the 1.5% Pd/Al$_2$O$_3$ catalyst with hydrazine hydrate solution at 50 °C for 10 min noticeably changed the appearance of the catalyst surface (Figs. 1 and 2). Although the surface of 1.5% Pd/Al$_2$O$_3$ with no reducer (Fig. 1) exhibits cracks, no single crystallites are detected even at 10 000× magnification. This indicates the presence of very fine Pd crystallites.
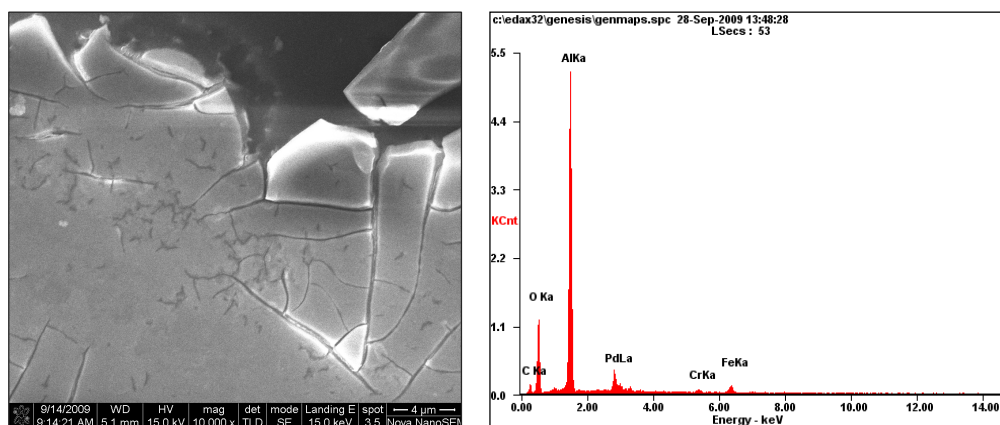

Fig. 1. SEM image (left) and results of X-ray microanalysis (right) of the surface of the 1.5% Pd/Al$_2$O$_3$ catalyst with no reducers; Pd precursor: Pd(NO$_3$)$_2$, magnification: 10 000×

After impregnation with hydrazine hydrate solution, the catalyst surface was covered with clusters of white crystallites. EDXS examinations have shown that Pd concentration in these crystallites is more than twice as high as in the grey fields on the catalyst surface (Fig. 2). White crystallites contain 6.05 at. % of Pd, 40.16 at. % of Al and 53.79 at. % of O, whereas in the dark fields of the surface 2.6 at. % of Pd, 45.9 at. % of Al and 51.5 at. % of O are found.
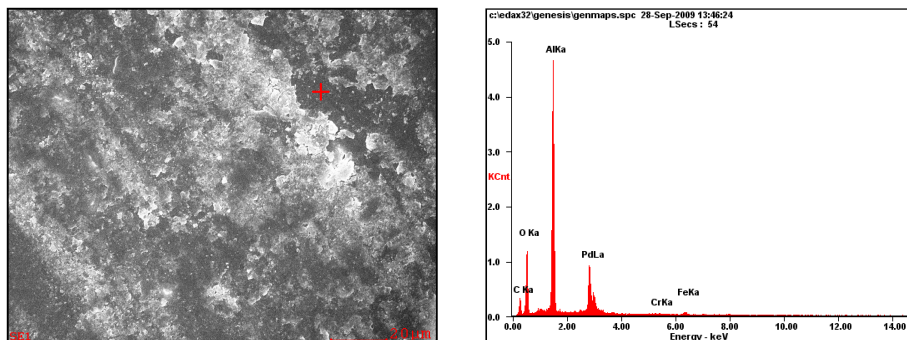

Fig. 2. SEM images and results of X-ray microanalyses of the surface of 1.5% Pd/Al$_2$O$_3$ catalyst impregnated with hydrazine hydrate solution at 50 °C for 10 min. Pd precursor: Pd(NO$_3$)$_2$

The XRD spectra of the 1.5% Pd/Al$_2$O$_3$ catalysts with no reducer addition and after 5 min impregnation with EDTA solution (Pd precursor: Pd(NO$_3$)$_2$), as well as the XRD spectra of the 1% Pd/Al$_2$O$_3$ catalyst (Pd precursor: PdCl$_2$), exhibit PdO peaks at 2Θ of 34° and peaks of heat-resisting FeCr20Al5 steel.
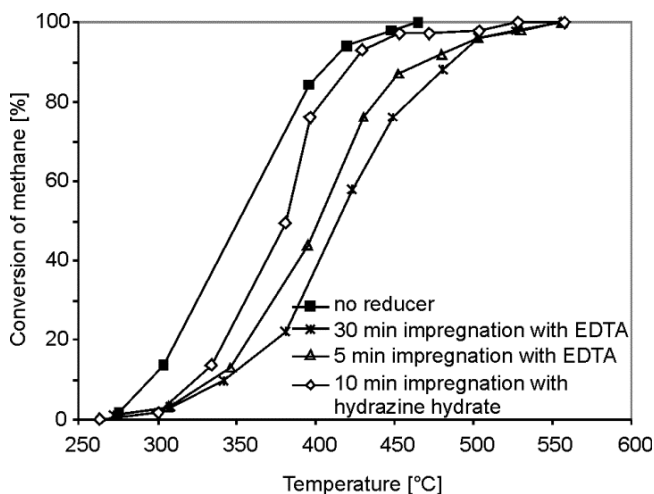

Fig. 3. Methane combustion activity of 1.5% Pd/Al$_2$O$_3$ catalysts with no reducer added, and after impregnation with EDTA and hydrazine hydrate

With Pd(NO$_3$)$_2$ as palladium precursor and in the absence of reducers, methane combustion efficiency increased when the Pd content increased from 1% to 1.5%. Over these catalysts, 100% conversion was achieved at 465 °C (1.5% of Pd) and 96% conversion at 509 °C (1% of Pd). Figure 3 shows temperature dependence of methane conversion over the 1.5% Pd/Al$_2$O$_3$ catalyst with Pd(NO$_3$)$_2$ as palladium precursor under the influence of EDTA or hydrazine hydrate addition. The activity of the catalyst was the highest when no reducing agent was added. Pd deposition onto the wash-coated support which was impregnated with 0.1 M EDTA solution for 5 min caused a substantial decrease in the catalyst activity despite the insignificant decrease in the size of PdO crystallites from 42 nm to 33 nm (XRD). Methane combustion efficiency decreased upon increasing the time of support impregnation. When the washcoated support was impregnated with hydrazine hydrate solution for 10 min, the decrease in the catalyst activity was lower than when EDTA solution was used.
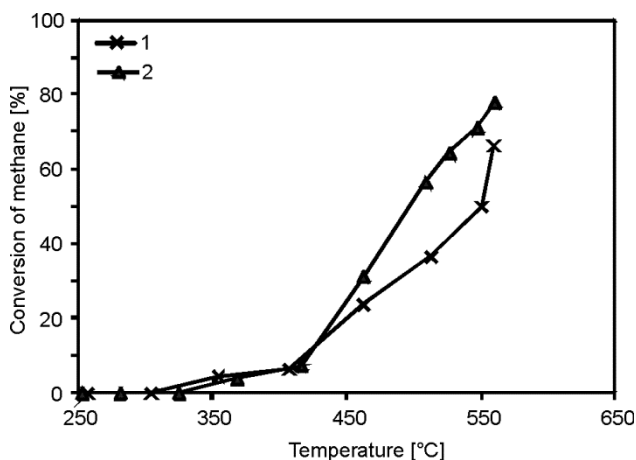

Fig. 4. Methane combustion activity of 1% Pd/Al$_2$O$_3$ catalysts prepared
by various methods: 1 – Pd deposited without 0.15% Al(OH)$_3$ sol,
2 – Pd deposited using Al(OH)$_3$ sol; palladium precursor: PdCl$_2$

When PdCl$_2$ was used as palladium precursor, methane combustion efficiency increased with the Pd content of the catalyst from 1% to 1.5%. Figure 4 shows the effect of the preparation method used on the activity of the monolithic 1% Pd/Al$_2$O$_3$ catalyst. Palladium was deposited onto the surface of the washcoat prepared from Al$_2$O$_3$ powder in mixture with aluminium hydroxide sol (0.15% Al(OH)$_3$) or without it. When use was made of the PdCl$_2$ precursor, the 1% Pd/Al$_2$O$_3$ catalyst where Pd was deposited together with the 0.15% Al(OH)$_3$ sol displayed a higher activity. In spite of this, its activity is noticeably lower as compared to the catalyst prepared with Pd(NO$_3$)$_2$ as the palladium precursor. This may be due to the poorer Pd dispersion and to the pres-

ence of larger Pd crystallites (Table 1) but also due to the poisoning effect of the chlorine persisting in the catalyst after calcination.
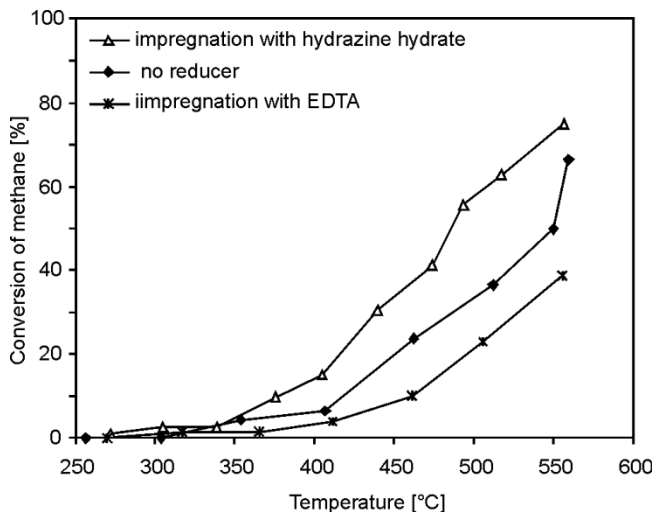

Fig. 5. Effect of the reducing agents (EDTA and hydrazine hydrate)
on the methane combustion activity of the 1% Pd/Al_2O_3 catalyst;
palladium precursor: $PdCl_2$, palladium deposited without $Al(OH)_3$ sol

With $PdCl_2$ as the palladium precursor and Pd deposition with no $Al(OH)_3$ sol, impregnation of the washcoated support with hydrazine hydrate solution improves the activity of the catalyst (compared to the catalyst with no reducer added). When the same catalyst is impregnated with 0.1 M EDTA solution, its activity decreases markedly (Fig. 5).

4. CONCLUSIONS

The catalysts show a noticeably higher methane combustion activity with palladium nitrate than with palladium chloride as the Pd precursor. Regardless of the Pd precursor applied, their activity increases with the increase in Pd content from 1% to 1.5%.

The activity of the catalysts depends on the preparation method used. With $PdCl_2$ as Pd precursor, the 1% Pd/Al_2O_3 catalyst where Pd was deposited together with the 1.5% $Al(OH)_3$ sol exhibited a higher methane combustion activity.

The addition of solution of hydrazine hydrate improves the activity of the 1% Pd/Al_2O_3 catalyst when use is made of $PdCl_2$ as the Pd precursor. With $Pd(NO_3)_2$ as the Pd precursor, methane combustion activity of the catalyst deteriorates.

The use of EDTA as a reducer decreases the activity of palladium-based catalysts irrespective of the Pd precursor applied.

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