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## EFFECT OF THE CeO<sub>2</sub> INGREDIENT ON THE ACTIVITY OF A Pd-BASED MONOLITHIC CATALYST FOR METHANE COMBUSTION

CeO<sub>2</sub> incorporation into Pd/Al<sub>2</sub>O<sub>3</sub> active phase enhanced thermal resistance of the catalyst and its activity in methane combustion. The activity of the catalyst depended on the amount of CeO<sub>2</sub> incorporated as well as on the method of incorporation and was found to be the highest in the 0.5%Pd/0.25%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 0.5%Pd/0.12%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 2%Pd/0.12%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> systems, where CeO<sub>2</sub> had been deposited onto the Al<sub>2</sub>O<sub>3</sub>-based washcoat. Methane conversion over such catalysts was notably higher than over 0.5%Pd/Al<sub>2</sub>O<sub>3</sub> and 2%Pd/Al<sub>2</sub>O<sub>3</sub>. The incorporation of CeO<sub>2</sub> into both washcoat and active layer brought about only a slight increase in the activity of the catalysts tested.

### 1. INTRODUCTION

Pd-based catalysts display very high activity in the combustion of methane [1]–[2]. Methane combustion is also catalyzed by metal oxides (Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, NiO, MnO, CeO<sub>2</sub>, CuO or Cr<sub>2</sub>O<sub>3</sub>) and by perovskites (ABO<sub>3</sub>) [3]–[5]. The catalytic activity of the transition metal oxides can be arranged in the following descending order: Co > Ni > Mn, Fe >> Cr [3].

Palladium catalysts used for the combustion of methane are usually supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> and MgO. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support is often doped with promoters like La<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, CaO, Cr<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub> and BaO, which raise the temperature of phase transition and prevent sintering [6], [7]. The incorporation of rare-earth element oxides (Ce, Pr, Nd, Sm) also increases the phase transition temperature of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and accounts for the thermal stability of the supported palladium [8]. What particularly contributes to the activity of the catalysts designed for combustion processes is the addition of CeO<sub>2</sub>, which not only reduces the proneness of aluminium oxide to sintering but also raises the stability of Pd dispersion on the support surface and diminishes the adverse influence of

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the sulphur carried by the flue gas [2]. CeO<sub>2</sub> has the ability to store oxygen in the case of its excess and to release it in the case of its deficiency, thus reducing the effect of rapid changes in the composition of the fuel–air mixture. Furthermore, CeO<sub>2</sub> is a promoter of the reaction of carbon oxide with water vapour and an inhibitor of the interaction of noble metals with the active forms of aluminium oxide [9]. The activity of the Pd catalyst in methane combustion can also be increased by the incorporation of Co<sub>3</sub>O<sub>4</sub> [10], NiO or SnO<sub>2</sub> [11] into the Al<sub>2</sub>O<sub>3</sub>-based support.

## 2. METHODS OF PREPARING CATALYSTS AND THEIR TESTING

The catalysts were prepared on monolithic supports made of a 00H20J5-type heat-resisting foil. The supports (70 mm in length and 26 mm in diameter, with triangular channels) were washcoated by the sol–gel method, CeO<sub>2</sub> being either added to Al<sub>2</sub>O<sub>3</sub> or deposited onto the washcoat. The washcoat surface was coated with 2 or 0.5 wt.% Pd. Use was also made of catalysts where CeO<sub>2</sub> was deposited together with Pd by impregnation of the washcoated support in a mixture of palladium and cerium nitrates at a Pd:Ce molar ratio of 4 to 9. After impregnation, the catalysts were calcined at 500 °C for 3 h. The catalysts manufactured for this study are characterized in the table.

Table

Characterization of the catalysts

Catalyst	Composition of washcoat (wt. %)	Amount of washcoat (wt. %)
0.5% Pd/Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	2.1
2% Pd/Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	1.9
2% Pd/Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> –1.1% CeO <sub>2</sub>	89.9% Al <sub>2</sub> O <sub>3</sub> 9% SiO <sub>2</sub> 1.1% CeO <sub>2</sub>	1.9
2% Pd/Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> –5.3% CeO <sub>2</sub>	86.1% Al <sub>2</sub> O <sub>3</sub> 8.6% SiO <sub>2</sub> 5.3% CeO <sub>2</sub>	2.1
2% Pd/0.12% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub>	0.12% CeO <sub>2</sub> covered with 90.9% Al <sub>2</sub> O <sub>3</sub> 9.1% SiO <sub>2</sub>	1.9
0.5% Pd/Al <sub>2</sub> O <sub>3</sub> –10% CeO <sub>2</sub>	90% Al <sub>2</sub> O <sub>3</sub> 10% CeO <sub>2</sub>	2.2
0.5% Pd/Al <sub>2</sub> O <sub>3</sub> –15% CeO <sub>2</sub>	85% Al <sub>2</sub> O <sub>3</sub> 15% CeO <sub>2</sub>	2.2
0.5% Pd/Al <sub>2</sub> O <sub>3</sub> –20% CeO <sub>2</sub>	80% Al <sub>2</sub> O <sub>3</sub> 20% CeO <sub>2</sub>	2.3
0.5% Pd/0.12% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.12% CeO <sub>2</sub> covered with Al <sub>2</sub> O <sub>3</sub>	2.2
0.5% Pd/0.25% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.25% CeO <sub>2</sub> covered with Al <sub>2</sub> O <sub>3</sub>	1.8
0.5% Pd/0.37% CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.37% CeO <sub>2</sub> covered with Al <sub>2</sub> O <sub>3</sub>	2.1
Pd–CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , Pd:Ce = 4	Al <sub>2</sub> O <sub>3</sub>	2.5
Pd–CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , Pd:Ce = 6.5	Al <sub>2</sub> O <sub>3</sub>	2.5
Pd–CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , Pd:Ce = 9	Al <sub>2</sub> O <sub>3</sub>	2.5

Methane combustion tests were carried out in a laboratory reactor heated electrically, with a programmed temperature ramp of 3<sup>o</sup>/min. The concentration of methane

accounted for 1 vol.% in air, gas hourly space velocity being set at 5800 h<sup>-1</sup>. Methane concentration was measured with a Sniffer analyzer (Bacharrach). A Monoxor I analyzer was used to measure CO concentration, a potential reaction by-product.

Investigations were also carried out into the resistance of the catalysts to thermal shocks. The samples were subjected to 4000 cycles of rapid heating up to 1000 °C and subsequent cooling down to room temperature. The change in the sample mass (after a certain number of cycles) compared to its initial value was regarded as a measure of resistance to thermal shocks.

### 3. RESULTS AND DISCUSSION

#### 3.1. CATALYST ACTIVITY

In this study, the influence of CeO<sub>2</sub> incorporated into the washcoat and active layer of the Pd-based monolithic catalyst on the efficiency of methane combustion was determined.

Figure 1 compares the methane conversion over catalysts with the palladium content of 2 wt.% in the active layer deposited onto the washcoats  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CeO<sub>2</sub> and over cerium dioxide deposited on the surface of the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> layer. The incorporation of 1.1 wt.% CeO<sub>2</sub> into the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-based washcoat increases methane conversion at the temperature lower than 460 °C. The coating of a washcoat surface with 0.12 wt.% CeO<sub>2</sub> (2% Pd/0.12% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst) raises methane conversion in the whole range of the temperature investigated compared to the 2% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Methane conversion in the presence of 2% Pd/0.12% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> does not decrease with the rise in the space velocity from 2900 to 5800 h<sup>-1</sup>, and remains stable for 100 h on stream.

A high price of palladium necessitates a reduction in the content of this noble metal in the catalyst. With these thoughts in mind, research was started to find out how the addition of CeO<sub>2</sub> would affect methane conversion over the catalysts with a 0.5 wt.% Pd content. As for the 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, the rise in methane conversion was noticeable when CeO<sub>2</sub> (0.12 or 0.25 wt.% CeO<sub>2</sub> content) was deposited onto the surface of the Al<sub>2</sub>O<sub>3</sub>-based washcoat. The highest activity was that of the 0.5% Pd/0.25% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The increase in CeO<sub>2</sub> content to 0.37 wt.% reduced methane conversion (figure 2). The incorporation of 10 to 20 wt.% CeO<sub>2</sub> into the Al<sub>2</sub>O<sub>3</sub>-based washcoat did not deteriorate its catalytic activity, and methane conversion over this catalyst is comparable with that over the 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

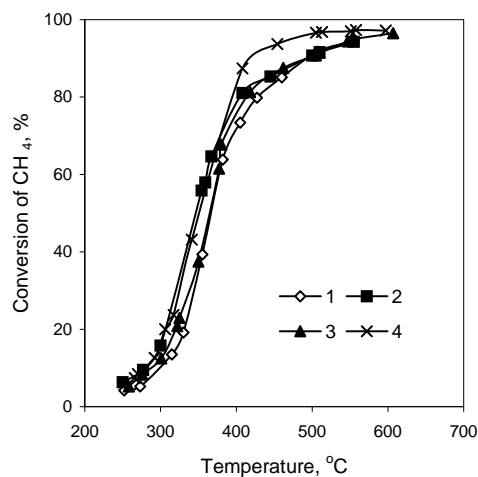


Fig. 1. Temperature-dependence of methane conversion over monolithic catalysts related to the amount of incorporated  $\text{CeO}_2$  and to the incorporation method. Catalysts: 1 – 2% Pd/ $\text{Al}_2\text{O}_3$ ; 2 – 2% Pd/ $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -1.1%  $\text{CeO}_2$ ; 3 – 2% Pd/ $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -5.3%  $\text{CeO}_2$ ; 4 – 2% Pd/0.12%  $\text{CeO}_2$ / $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$

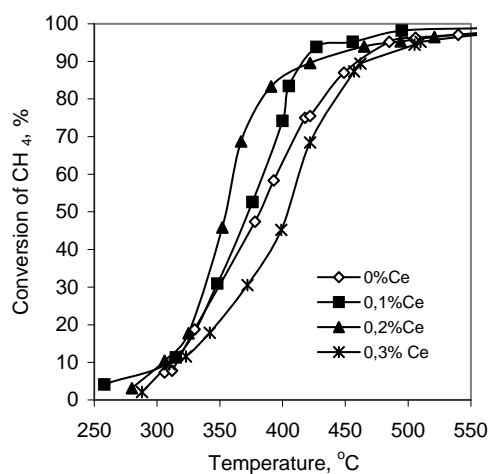


Fig. 2. Temperature-dependence of methane conversion over 0.5% Pd/ $\text{CeO}_2$ / $\text{Al}_2\text{O}_3$  related to cerium content ( $x\%$  Ce)

Attempts were also made to incorporate  $\text{CeO}_2$  into the active layer of the 0.5% Pd/ $\text{Al}_2\text{O}_3$  catalyst. Thus, the activity of the catalyst was found to increase as the Pd:Ce molar ratio in the active layer increased. At temperature higher than 420 °C and a Pd:Ce molar ratio of 9, methane conversion was higher compared to that in the presence of 0.5% Pd/ $\text{Al}_2\text{O}_3$  catalyst.

## 3.2. CATALYST RESISTANCE TO THERMAL SHOCKS

Methane combustion involves a high temperature, and that is why the problem of catalyst resistance to thermal shocks has gained in importance. The catalysts were exposed to alternate heating and cooling to examine their resistance to thermal shocks, which provided an accelerated aging at high temperature. Alternate heating to the temperature of 1000 °C and cooling down to ambient temperature make the catalyst expand and shrink. As there are differences in the thermal expansion between the metal, the washcoat and the catalytic layer, it can be expected that particular layers will suffer cracking and fall off from the support. The loss of catalyst mass during thermal shocks may be due to the reduction of PdO to metallic Pd at temperature exceeding 780 °C. As for the catalyst with the 2 wt.% Pd content, mass decrease may approach 0.3%. In all the catalysts containing  $\text{CeO}_2$ , mass decrease after thermal shocks is lower than in the Pd/ $\text{Al}_2\text{O}_3$  catalysts containing 2 and 0.5 wt.% Pd (figures 3 and 4). After 3600 cycles of heating and cooling, relative loss of mass in the 2% Pd/0.12% Ce/ $\text{Al}_2\text{O}_3$  and 2% Pd/ $\text{Al}_2\text{O}_3$  catalysts amounts to 0.12% and 0.72%, respectively (figure 3). As for the 0.5% Pd catalyst, relative loss of mass is observed at the beginning and is followed by a gradual mass increase up to the initial value. In all 0.5% Pd catalysts with a  $\text{CeO}_2$  ingredient, mass decrease is lower than in the 0.5% Pd/ $\text{Al}_2\text{O}_3$  catalyst (figure 4). A smaller mass loss in the catalysts with a  $\text{CeO}_2$  ingredient than in those without it may prove that, at increased temperature, the presence of  $\text{CeO}_2$  inhibits the reduction of PdO to metallic Pd on the catalyst surface.

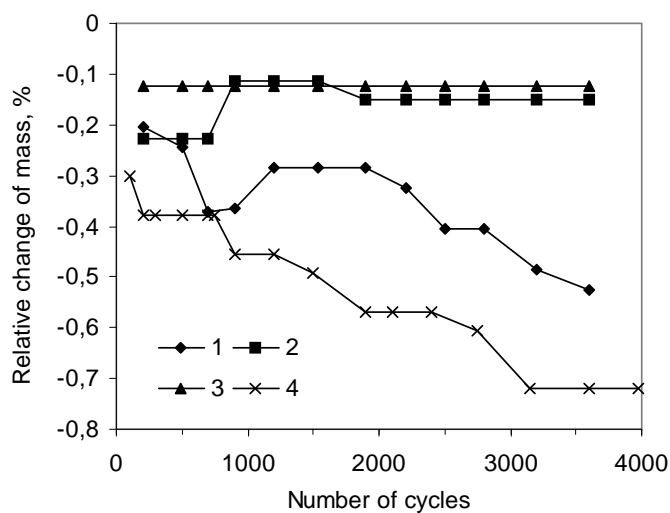


Fig. 3. Pd-based (2 wt.%) catalyst resistance to thermal shocks:  
 1 – 2% Pd/ $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ –1.1%  $\text{CeO}_2$ ; 2 – 2% Pd/ $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ –5.3%  $\text{CeO}_2$ ;  
 3 – 2% Pd/0.12%  $\text{CeO}_2$ / $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ ; 4 – 2% Pd/ $\text{Al}_2\text{O}_3$

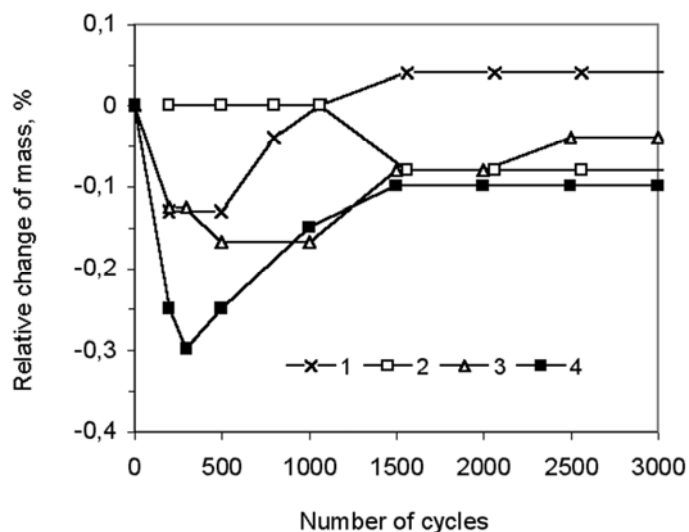


Fig. 4. Pd-based (0.5 wt.%) catalyst resistance to thermal shocks:  
 1 – 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>–10% CeO<sub>2</sub>; 2 – 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>–15% CeO<sub>2</sub>;  
 3 – 0.5% Pd/0.25% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; 4 – 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>

#### 4. CONCLUSIONS

The incorporation of CeO<sub>2</sub> into Pd-based monolithic catalysts increases methane conversion. Irrespective of whether the catalyst has a 2 or 0.5 wt.% Pd content, its catalytic activity is very high when CeO<sub>2</sub> is deposited onto the surface of the Al<sub>2</sub>O<sub>3</sub>-based washcoat. The highest conversion of methane was observed over the 0.5% Pd/0.25% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 0.5% Pd/0.12% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 2% Pd/0.12% CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Their activity was noticeably higher than that of the catalysts without the CeO<sub>2</sub> ingredient, and they all showed a high resistance to thermal shocks.

The addition of a small amount of CeO<sub>2</sub> (Pd:Ce = 9) into the Pd-containing active layer enhances the conversion of methane at elevated temperature.

The incorporation of a 10 to 20% CeO<sub>2</sub> ingredient into the Al<sub>2</sub>O<sub>3</sub>-based washcoat has no effect on the activity of the 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The incorporation of CeO<sub>2</sub> into the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst results in a diminished reduction of PdO to metallic Pd at the temperature higher than 780 °C.

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WPLYW DODATKU CeO<sub>2</sub> NA AKTYWNOŚĆ  
MONOLITYCZNEGO KATALIZATORA PALLADOWEGO PODCZAS SPALANIA METANU

Badanie aktywności katalizatorów palladowych z dodatkiem tlenku ceru(IV) podczas spalania metanu wykazało, że tlenek ten zwiększa aktywność katalizatora Pd/Al<sub>2</sub>O<sub>3</sub>. Aktywność katalizatorów zależy od sposobu wprowadzenia CeO<sub>2</sub> i jego ilości. Najwyższą aktywność wykazują katalizatory o składzie 0,5% Pd/0,2% Ce/Al<sub>2</sub>O<sub>3</sub>, 0,5% Pd/0,12% Ce O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> i 2% Pd/0,12% Ce O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, w których CeO<sub>2</sub> naniesiono na powierzchnię warstwy pośredniej z Al<sub>2</sub>O<sub>3</sub>. Uzyskuje się na nich stopień przereagowania metanu znacznie wyższy niż na katalizatorach odpowiednio 0,5% Pd/Al<sub>2</sub>O<sub>3</sub> i 2% Pd/Al<sub>2</sub>O<sub>3</sub>. Wprowadzenie CeO<sub>2</sub> do warstwy pośredniej i warstwy aktywnej katalizatora powoduje tylko niewielki wzrost jego aktywności.