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METHANE COMBUSTION OVER MONOLITHIC CATALYSTS

Palladium and/or metal oxide catalysts (SnO_2 or ZrO_2 alone or doped with palladium) as well as one $LaMnO_3$ perovskite catalyst were tested for activity during low-temperature methane oxidation. All the catalysts were on monolithic metallic supports washcoated with γ-Al_2O_3. Palladium was incorporated into the active phase either during the final preparation procedure by deposition onto the alumina and metal oxide coated supports (MeO + Pd), or by dipping the washcoated supports in slurries of appropriate metal oxide with palladium acetate (Me/Pd). Palladium and SnO_2 + Pd catalysts displayed the highest activity in methane combustion, and in the presence of those catalysts methane conversion reached 90% at 365 °C and 320 °C, respectively. In the repeated test of methane combustion, almost all the catalysts showed a loss in activity. The low stability of the catalysts may be due to the insufficient amounts of the active ingredients, especially palladium.

1. INTRODUCTION

The substantial greenhouse effect produced by methane makes it necessary to control its anthropogenic emissions, particularly from the vehicles fuelled by natural gas and power plants. The problem of ever increasing methane emissions from lean fuel burning, especially in heavy-duty vehicles, can be attributed to a continual rise in the number of cars fuelled in this way. On the other hand, the process of power generation by catalytic combustion of natural gas, conducted at significantly lower temperatures (1200–1400 °C) than those of thermal combustion, is environmentally-friendly because of a much lower emission of nitrogen oxides, the other air pollutants having a number implications for both human health and natural environment. Other sources of anthropogenic methane emissions include animal farms, biological processes allowing solid waste disposal, wastewater treatment, coke and biomass combustion, etc.

Methane, the simplest saturated alkane, is the most difficult hydrocarbon to oxidize catalytically and requires much higher reaction temperatures than do other organic

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compounds. The choice of the catalyst system depends on the range of the process temperature and the composition of the gas combusted. Noble metal and transition metal oxides are widely tested in methane combustion. The advantage of noble metals over metal oxides is their high specific activity, which results from high metal dispersion on conventional supports (like alumina or silica) with large specific surface area. For this reason, they are preferably applied to low-temperature methane combustion, although metal oxide systems, being less active than noble metals, are more attractive in economical terms. As for high-temperature processes, extensive research has been reported into catalysts based on hexaaluminates ($AMnAl_{11}O_{19-\gamma}$, where A = La, Pr, Sm, Nd, or $Sr_xLa_{1-x}Al_{12}O_{19}$), which are of very high thermal stability [1], [2]. Of the noble metals, palladium has been found to be particularly suited for methane combustion [1], [3], [4]. Those high-activity catalysts, however, undergo thermal deactivation at elevated temperatures (metal and support sintering; phase transformation) or chemical deactivation in the presence of chlorine or sulphur compounds as well as water vapour in the combusted gases.

It has been found that a greater resistance to both thermal and chemical deactivation is inherent in catalytic systems involving palladium and some metal oxides, e.g., ZrO_2, SnO_2, CeO_2 or MgO, doped to the active phase or support [5]–[7]. Ceria is known for its ability to store oxygen. Added to the alumina support, ceria inhibits changes in the alumina structure and maintains good dispersion and activity of a metal catalyst. Zirconia enhances the mobility of lattice oxygen in the catalyst structure, thus increasing overall catalytic activity.

The aim of the present study was to produce metal-supported monolithic catalysts based on palladium or metal oxide (ZrO_2 and SnO_2) alone or on either ZrO_2 or SnO_2 doped with palladium. In addition, an $LaMnO_3$ perovskite-based catalyst was prepared for comparative purposes. Their activity was tested during methane combustion.

2. METHODS

2.1. PREPARATION OF CATALYSTS

Eight catalysts (Pd, ZrO_2, SnO_2 or $LaMnO_3$ based) on monolithic metallic supports from heat-resisting alumel steel (Fe–Cr–Al alloy) were prepared for the purpose of the study. After chemical pretreatment (etching in sulphuric acid solution), the monolithic supports, formed from corrugated and flat foils, were washcoated with γ-Al_2O_3 by the Makarov method, i.e., by immersion in NaOH solution with aluminium chips at 60 °C for 5 h and thereafter at room temperature for 24 h. Upon drying and calcination, the mass of the alumina washcoat approached 6 wt.%. The supports prepared in this way

were coated with active phases by dipping them in slurries which contained the appropriate active ingredient: SnO_2, ZrO_2 or $LaMnO_3$ perovskite. Palladium was added from the $Pd(CH_3COO)_2$ and ethanol solution.

Palladium-doped catalysts were produced using two different methods. In one of them, palladium was incorporated in a final preparation procedure by deposition onto the support which had been washcoated with $γ$-Al_2O_3 and then with ZrO_2 or SnO_2 (Me + Pd). In the other method, the solution of palladium acetate and ethanol was added to the slurry of an appropriate metal oxide, and the active ingredients were deposited altogether onto the $γ$-Al_2O_3-washcoated support. All the catalysts had a diameter of 21 mm, the height of P1, P2, P5 and P8 amounted to 25 mm, whereas that of the remaining catalysts was 50 mm.

The composition of the active layers of each catalyst is shown in the table.

T a b l e

Composition of the catalysts

| Catalyst | Increment in the mass of the active ingredient, wt.% | |
	Sample 1	Sample 2
P1 ($LaMnO_3$)	10.1	10.5
P2 (SnO_2)	11.2	13.9
P3 (SnO_2 + Pd)	5.8 (0.0174% of Pd)	7.2 (0.0216% of Pd)
P4 (SnO_2/Pd)	3.7 (0.0111% of Pd)	2.4 (0.0072% of Pd)
P5 (ZrO_2)	28.3	20.9
P6 (ZrO_2 + Pd)	18.4 (0.0552% of Pd)	16.8 (0.0504% of Pd)
P7 (ZrO_2/Pd)	5.8 (0.0177% of Pd)	4.9 (0.0147% of Pd)
P8 (Pd)	0.3	0.3

The values of palladium content in parentheses refer to the overall catalyst mass.

2.2. LABORATORY SETUP FOR CATALYST ACTIVITY TESTS

The tests of catalyst activity in the process of methane combustion were performed in an eletrically heated quartz reactor. Temperature was measured with a thermocouple placed just before the catalyst and controlled by varying the current intensity with a transformer. Reaction temeperature ranged from 150 to 450 °C. Methane was supplied from a cylinder through a flow-control unit and mixed with compressed air in a mixer filled with inert glass rings. Both gas streams were controlled by an electronic mass flowmeter. Methane concentration was analyzed by gas chromatography; inlet and outlet gas samples for analysis being taken automatically. The inlet concentration of methane was 0.53 vol.%. The flow rate of the reaction mixture was constant (14 dm^3/h). Depending on the size of the catalyst sample tested, this gave two

space velocities, i.e., 810 h^{-1} and 1620 h^{-1}, for catalysts of 50 mm and 25 mm height, respectively.

3. RESULTS

As already mentioned, the catalysts differed in height, and the flow of the reaction mixture was constant, which had an immediate impact on the space velocity to be used. Thus, the catalysts P1, P2, P5 and P8 were tested at a space velocity of 1620 h^{-1}, and the other four at 810 h^{-1}. The temperature dependence of methane conversion over particular catalysts is plotted in figure 1.

*- Space velocity 1620 h^{-1}
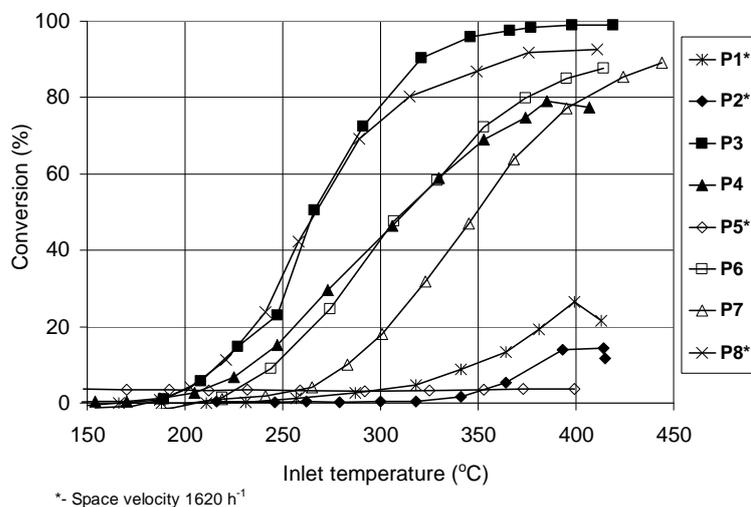
Fig. 1. Methane conversion over the catalysts tested versus temperature

As shown by these plots, the catalysts P3 and P8 were most active in a whole range of the temperature applied. In their presence, 50% methane conversion was attained at 265 °C. As for the other catalysts, 50% conversion was reached at a temperature that was higher by about 50 °C over P4 or P6, and by about 80 °C in the presence of P7. However, 90% conversion was achieved only over P3, P8 or P7 at 320 °C, 370 °C and 450 °C, respectively. Very poor catalytic activities were those of P2 and P6 (with SnO_2 and ZrO_2 alone, respectively, as the active phase), over which methane conversion did not exceed 17%. The catalytic activity of P1 (the $LaMnO_3$ perovskite catalyst) proved to be only slightly higher, as in its presence the maximal conversion amounting to 26% was achieved at 400 °C.

*- Space velocity1620 h⁻¹
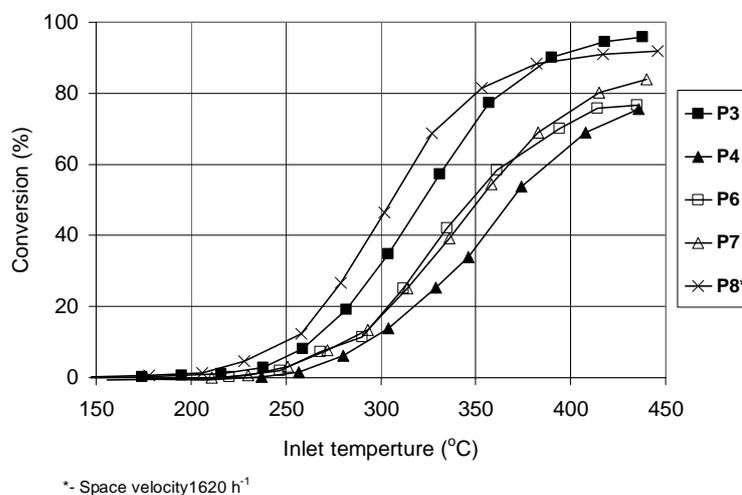
Fig. 2. Methane conversion over the most active catalysts of series I versus temperature

In order to determine the stability of the best catalysts of the first measuring series, the methane combustion test was repeated. The results are shown in figure 2. As can be seen from these plots, the activity of each of the catalysts tested decreased compared to series I. Again, P8 and P3 were found to be the most active with a 50% methane conversion at 305 °C and 325 °C, respectively. Compared to the temperatures of 50% conversion in series I, they are by 40 °C and 60 °C higher. P3 and P8 are also the catalysts over which methane conversion exceeds 90%. As in series I, 90% conversion was not attained with the other catalysts.

4. SUMMARY

The analysis of an available literature on catalytic combustion of methane substantiates the highest activity of palladium in this type of reaction, and so do the results of our tests. Of the monolithic catalysts tested, the one with 0.3 wt.% of Pd alone as the active layer (P8) was found to display the highest catalytic activity. The SnO_2 + Pd catalyst, with palladium deposited onto the SnO_2 layer (P3), was only slightly less active compared to P8. It should, however, be noted that the methane combustion tests over P3 were carried out at a space velocity which was half the one applied in the presence of P8. The catalysts with ZrO_2 as the active ingredient (alone or doped with palladium) as well as the $LaMnO_3$ perovskite catalyst showed a lower activity in methane combustion.

When the methane combustion test was repeated, there was a notable drop in catalytic activity with one exception; the ZrO_2/Pd catalyst, where palladium had been add-

ed to the ZrO_3 suspension (P7), retained almost the same activity. A reduced activity of all other catalysts substantiates the need of optimizing the method of their preparation, which is particularly difficult when the catalysts are deposited onto monolithic metal supports. The poor stability of the catalysts may also be due to the insufficient amount of palladium in the active phase.

ACKNOWLEDGEMENTS

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SPALANIE METANU NA KATALIZATORACH MONOLITYCZNYCH

Przedstawiono wyniki spalania metanu na monolitycznych katalizatorach metalicznych, których głównymi składnikami były: perowskit ($LaMnO_3$), pallad oraz SnO i ZrO_2, samych i z dodatkiem palladu. Pallad wprowadzano do fazy aktywnej dwiema metodami – w pierwszej nanosząc go na już istniejącą warstwę tlenków SnO_2 bądź ZrO_2, a w drugiej nanosząc związki palladu w mieszaninie z tlenkami. Najwyższą aktywność wykazały katalizatory z samego palladu oraz SnO_2 + Pd i jedynie na nich uzyskano 90% spalanie metanu odpowiednio w temperaturze 320 i 365 °C. Powtórny test spalania metanu wykazał spadek aktywności niemal wszystkich katalizatorów. Brak ich stabilności może wynikać ze zbyt małej ilości czynnika aktywnego.