Catalysis Today 137 (2008) 324–328

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of washcoat modification with metal oxides on the activity of a monolithic Pd-based catalyst for methane combustion

Barbara Kucharczyk, Włodzimierz Tylus *

Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology, Wybrzeże St. Wyspiańskiego 27, 50-370 Wrocław, Poland

ARTICLE INFO

Article history:
Available online 14 July 2008

Keywords:
Methane combustion
Monolithic catalyst
Washcoat

ABSTRACT

The deposition of Ni, Co, Ce or Fe oxides onto the washcoat surface in the 0.5%Pd/Al_2O_3 catalyst enhances conversion of CH_4. Catalytic activity of the Pd-catalysts containing cobalt oxide depends on the incorporated amount of cobalt oxide and the method of incorporation. The highest activities were those of the 0.5%Pd/0.3%Co/Al_2O_3 and 1%Pd/0.3%Co/Al_2O_3 catalysts (cobalt oxide deposited onto the surface of Al_2O_3) and the 0.5%Pd/5%Co_3O_4–Al_2O_3 catalyst (mixed washcoat). Total SSA, Pd dispersion and Pd crystallite size in the *x*%Pd/*y*%Co/Al_2O_3 catalysts depend on the incorporated amount of PdO and cobalt oxide. Pd dispersion in the 1%Pd/Al_2O_3 catalyst increases from 4% to 20% upon deposition of 14 wt.% Co_3O_4 (by mass Al_2O_3) onto the Al_2O_3 surface (1%Pd/0.3%Co/Al_2O_3). This increase in Pd dispersion influence the increase in the activity of the 1%Pd/Al_2O_3 catalyst. On the surface of the 0.5%Pd/5%Co_3O_4–Al_2O_3 catalyst Pd occurs mainly in the form of PdO and displays considerable mobility under conditions of temperature variations—cyclically undergoing reduction and oxidation. At 500 °C, in vacuo, the reduction was irreversible and parallelled by the agglomeration of metallic Pd crystallites. At room temperature, cobalt occurred on the catalyst surface in the form of Co^{+2} ions ($CoAl_2O_4$) and was reduced to Co^0 at 500 °C (in vacuo). Up to 500 °C, the reduction of Co was reversible.

1. Introduction

A Pd-based catalyst shows a very high activity in the combustion of methane [1–7]. Pd-catalysts are usually supported on Al_2O_3, SiO_2, TiO_2 or MgO. To increase the phase transition temperature of γ-Al_2O_3 and provide for the thermal stability of PdO, it is conventional to incorporate La_2O_3, Li_2O, CaO, Cr_2O_3, MgO, ZrO_2 or BaO [2,3], as well as add some rare earth oxides (Ce, Pr, Nd or Sm) [4,5]. The activity of the Pd-based catalyst for methane combustion can be enhanced by the addition of NiO [6–8], SnO_2 [6] or Co_3O_4 [1,7] into the Al_2O_3. Compared to Pd/Al_2O_3, the Pd/Al_2O_3–Co_3O_4 catalyst displays a higher activity in methane combustion [7–9]. The activity of Pd/Al_2O_3–Co_3O_4 depends strongly on the Co_3O_4 content [7]. Very active in CH_4 combustion are Pt and Au deposited onto Co_3O_4 [10].

In this work we examined the effect of washcoat modification with Co, Ni, Ce, Fe, Cu, Mn, Cr oxides on the activity of monolithic Pd/Al_2O_3 catalyst, with emphasis on the effect of cobalt oxide on the physicochemical properties (XPS, BET) and activities in CH_4 combustion. Our study also aimed at comparing the activities of the catalysts in methane combustion when Pd was deposited onto Al_2O_3 (0.5%Pd/Al_2O_3 catalysts); onto cobalt oxide (0.5%Pd/*x*%Co/Al_2O_3 catalysts), and onto a mixed cobalt oxide–alumina layer (0.5%Pd/*x*%Co_3O_4–*y*%Al_2O_3 catalysts).

2. Methods of catalysts preparation and investigation

Monolithic catalysts were prepared on a support made of heat-resisting FeCr20Al5 foils (thickness of 0.05 mm), cylindrically wound (70 mm in length and 26 mm in diameter), with a honeycomb cross-section. The channels of the monolith (112 per square centimetre) were triangular in shape (the side of the triangle being 1.4 mm long). The monolithic support was wash-coated with Al_2O_3 or mixed oxides (Al_2O_3 with 5–15% Co_3O_4) by the sol–gel method and calcined at 400 °C for 3 h. The sol was prepared by mixing calculated amounts of $Al(OH)_3$ (obtained by the hydrolysis of aluminium isopropoxide (Aldrich)), glycerol, distilled water and $Co(NO_3)_2{\cdot}6H_2O$ (Fluka). Then the sol was treated with a buffer solution until the pH of 7.5 was achieved, and stirred at a rate of 500 rpm at room temperature for 2 h to obtain a stable sol. The monolithic support was immersed in the sol, dried at room temperature for 4 h and thereafter at 110 °C for 3 h, and subsequently calcined at 400 °C for 3 h. The amount of the washcoat was 2.2 ± 0.1 wt.% in relation to the support mass. Catalysts were also prepared with Al_2O_3 washcoats covered with

---

* Corresponding author. Tel.: +48 71 320 35 95; fax: +48 71 328 04 25.
E-mail address: wlodzimierz.tylus@pwr.wroc.pl (W. Tylus).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.05.018

Table 1
Characterization of the catalysts and washcoat powders

Catalyst	Composition of washcoat (wt.%)	SSA of washcoat powders (m^2/g)	Total SSA[a] of catalyst (m^2/g_{cat})	Active metal surface area[a] (m^2/g_{cat})	Percent dispersion of Pd[a] (%)	Average size of Pd crystallites[a] (nm)
Al_2O_3/support	Al_2O_3	349	8.9	–	–	–
0.5%Pd/Al_2O_3	Al_2O_3	349	5.6	0.15	14.0	8.0
0.5%Pd/0.2%Co/Al_2O_3	Al_2O_3 covered with 13%[b] Co_3O_4	279	4.0	0.14	13.1	8.6
0.5%Pd/0.3%Co/Al_2O_3	Al_2O_3 covered with 17.8%[b] Co_3O_4	248	2.9	0.14	11.3	9.9
0.5%Pd/0.4%Co/Al_2O_3	Al_2O_3 covered with 22.7%[b] Co_3O_4	225	5.2	0.19	12.0	9.3
1%Pd/Al_2O_3	Al_2O_3	349	1.3	0.01	3.8	29.6
1%Pd/0.3%Co/Al_2O_3	Al_2O_3 covered with 14%[b] Co_3O_4	248	3.3	0.35	20.3	5.5
0.5%Pd/5%Co_3O_4–Al_2O_3	5% Co_3O_4, 95% Al_2O_3	370	–	0.14	12.6	8.9
0.5%Pd/10%Co_3O_4–Al_2O_3	10% Co_3O_4, 90% Al_2O_3	323	–	0.16	13.9	8.0
0.5%Pd/15%Co_3O_4–Al_2O_3	15% Co_3O_4, 85% Al_2O_3	312	–	–	–	–

[a] Measurements were performed using samples of washcoated supports covered with palladium.
[b] Proportion of Co_3O_4 mass to Al_2O_3 mass in the catalyst.

the nitrates of Co (Fluka), Ni, Ce and Fe (POCH) (0.1% metal by support mass) and calcined at 500 °C for 3 h. Catalyst surfaces were impregnated with $Pd(NO_3)_2$ to deposit 0.5% Pd or 1% Pd in relation to the support mass, and calcined at 500 °C for 3 h. In those catalysts, Pd content amounted to 4.5 g and 9 g per 1 dm^3 of catalyst, at Pd 0.5% and Pd 1%, respectively. The characterization of the catalysts is included in Table 1.

Surface composition was analyzed by X-ray photoelectron spectroscopy (XPS), using a SPECS UHV system equipped with a PHOIBOS 100 spectrometer and SpecLab software. The X-ray source was generated with an Al anode operating at 100 W (survey scan) and 200–300 W (high resolution spectra). The analyzer mode was set at constant pass energy (30 eV, survey scan; 5 eV, narrow scan). The C 1s line (284.6 eV) was taken as a reference to correct electrostatic charging. The residual pressure in the chamber was below 5×10^{-10} mbar with hydrogen as the main component of the gas phase (>90%, vol.). The detection angle was normal to the sample surface (8 mm × 8 mm).

BET specific surface areas (SSA) of washcoat powders were measured from nitrogen sorption by the static volumetric method at liquid nitrogen temperature, using Autosorb-1C Quantachrome (repeatability ±3%). The SSA values of the catalysts with metal supports were determined by the same method, using ASAP 2405N V.101 (repeatability ±4%). Active metal surface area and dispersion of palladium were calculated on the basis of total hydrogen chemisorption at 110 °C, using Autosorb 1CMS Quantachrome (repeatability ±0.92% dispersion). Prior to the estimation of metal dispersion, the samples were made subject to the following pretreatment: heating in hydrogen stream to the temperature of 110 °C (20°/min) and reduction with hydrogen for 1 h, evacuation at 110 °C for 20 min and at 300 °C for 2 h, cooling to 110 °C for 1 min and evacuation for 10 min. The isotherm of hydrogen chemisorption was determined over the pressure range of 20–200 mmHg, at a chemisorption stoichiometry H/Pd = 1 and at cross-section areas of hydrogen and Pd amounting to 10.41 Å and 7.874 Å, respectively. Dispersion (D_{Pd}) was calculated in terms of the formula $D_{Pd} = m_H/n_{Pd}$ (m_H, number of H atoms chemisorbed on 1 g of catalyst; n_{Pd}, number of Pd atoms in 1 g of catalyst), the mean size of Pd crystallites (in nm) being computed in terms of the formula $d_{Pd} = 1.12/D_{Pd}$.

Catalytic activity was tested in the combustion of 1% CH_4 in air, using a flow reactor (i.d., 26 mm; length, 400 mm) placed in a heater (heating ramp, 3 °C/min), gas flow velocity being set to 5800 h^{-1} on the total monolith volume. The reaction of methane combustion was stabilized for 20 min in the temperature required. The methane conversion values obtained are arithmetic means from three measurements. Methane concentrations were measured with a Sniffer methane analyzer (Bacharach, repeatability 5% relative).

3. Results and discussion

3.1. XPS measurements

Calcination of Al_2O_3 impregnated with Co^{+2} salts induces the formation of three main Co species: bulk Co_3O_4, Co^{+2} ions in tetrahedral sites ('surface-like spinels') and Co^{+2} ions in octahedral sites ('surface-like CoO') [11]. The distribution of these species on the surface depends on the cobalt content and calcination temperature – inc calcination temperatures favours the formation of Co^{+2} ions in tetrahedral sites, i.e. well-dispersed surface phase, similar to $CoAl_2O_4$ [12]. XPS analyses of 0.5%Pd/x%Co/Al_2O_3 catalysts confirm the findings reported in the literature (Fig. 1). Co 2p scans substantiate primarily the presence of the Co^{+2} ions ascribed to the $CoAl_2O_4$ spinel. For the 0.5%Pd/0.3%Co/Al_2O_3 catalyst, binding energy was estimated at 781.1 eV (as was the case with $CoAl_2O_4$), although the slight broadening of the Co $2p_{3/2}$ peak and the shift in the position of Co $2p_{1/2}$ by approx. 0.2 eV towards lower energies suggest the presence of some Co_3O_4. It is essential to note that a broadening of the peak is also observed on the side of lower energies, which indicates that insignificant amounts of CoO are present (BE 779.7 eV; Fig. 1b).

Palladium was found to occur in the form of PdO on the surfaces of the fresh 0.5%Pd/x%Co/Al_2O_3 and 0.5%Pd/x%Co_3O_4–Al_2O_3 catalysts. The BE values of Pd $3d_{3/2}$ for these catalysts were assessed to 336.55 ± 0.1 eV; they approached the BE value of 336.7 eV for PdO in Pd/Al_2O_3 (dotted line in Fig. 2). It is well known that the incorporation

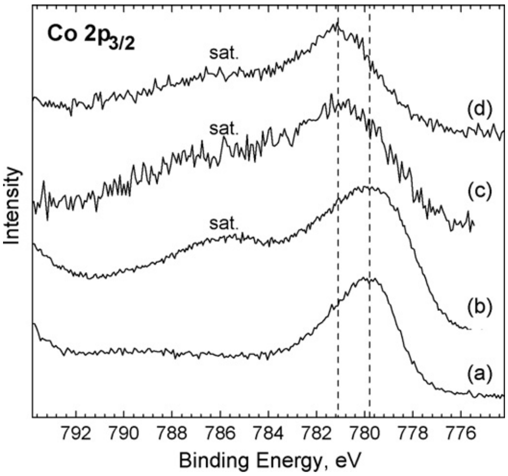

Fig. 1. XPS Co 2p spectra for Co_3O_4 (a), CoO (b), 0.5%Pd/0.3%Co/Al_2O_3 (c), and $CoAl_2O_4$ (d).

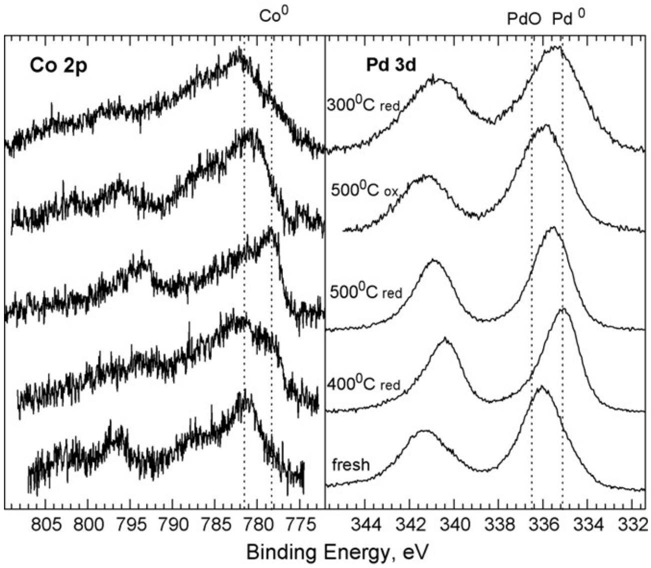

Fig. 2. XPS Co 2p and Pd 3d spectra for 0.5%Pd/5%Co_3O_4–Al_2O_3 catalyst at different temperatures (UHV).

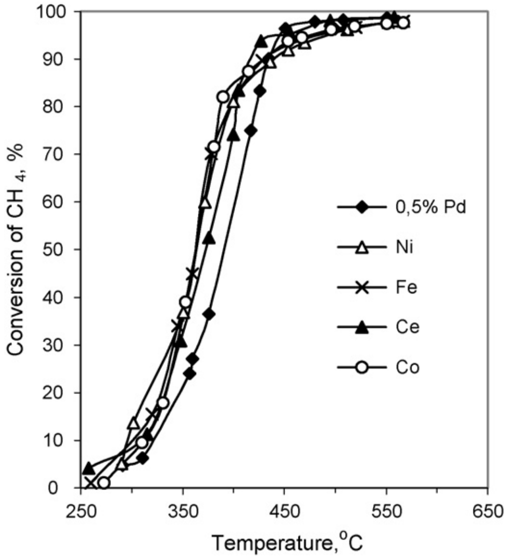

Fig. 3. Conversion of methane over 0.5%Pd/0.1%M/Al_2O_3 (M = Ni, Fe, Ce, Co) catalysts.

of Pd into Co catalysts can considerably affect the reduction of Co oxides [13]. The ability to reduce and re-oxidate Co exerts an influence on the selectivity and activity of the catalyst. Fig. 2 shows the cyclic variations in the extent of cobalt and palladium oxidation at different temperatures under reducible residual gases in the UHV XPS chamber for the 0.5%Pd/Al_2O_3–x%Co_3O_4 catalysts. From these plots it can be inferred that cobalt alone is reducible only at high temperatures, not applied here. In the case of Pd on mixed-washcoat (Al_2O_3–Co_3O_4) catalysts, a noticeable reduction of Co^{+2}–Co^0 occurred at 300 °C; at 500 °C, the spectrum revealed the dominance of metallic cobalt. In UHV conditions, PdO reduces at approx. 200 °C [5], and at 400 °C only the Pd^0 phase has been observed. At higher temperatures, Pd became sintered irreversibly, and formed larger crystallites of metallic Pd covered with a PdO layer (it is to be noted that such UHV conditions corresponded to those of catalyst ageing). Agglomeration of Pd is substantiated by the decrease in the Pd/Co and Pd/Al ratios with the rise in temperature.

3.2. Catalyst activity testing

We examined the effect of washcoat modification with Ni, Ce, Co, Fe, Cu, Mn, Cr or La oxides (0.1% metal by weight) on the activity of the monolithic Pd/Al_2O_3 catalyst. Thus, at temperatures lower than 550 °C, catalytic activity was found to deteriorate when Cu, Mn, Cr or La oxides were added. The activity of the catalysts obtained can be ordered as follows: Pd/Al_2O_3 > Pd/La_2O_3 > Pd/MnO > Pd/CuO > Pd/Cr_2O_3. The addition of Ni, Co, Ce or Fe oxides enhanced the activity of the 0.5%Pd/Al_2O_3 catalyst for CH_4 combustion at temperatures below 400 °C (Fig. 3). When

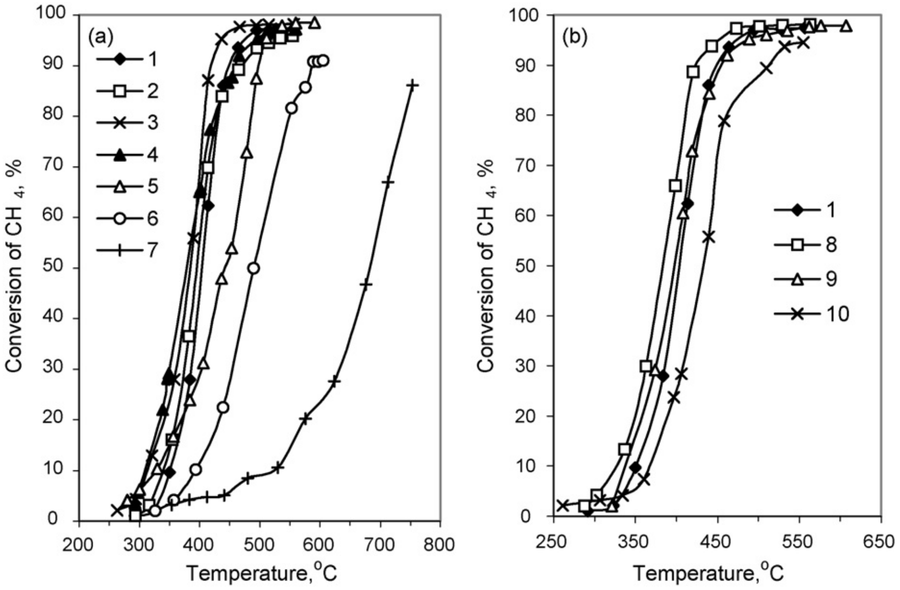

Fig. 4. Catalytic combustion of methane over 0.5%Pd/x%Co/Al_2O_3 (a) and 0.5%Pd/x% Co_3O_4–Al_2O_3 (b) catalysts with different cobalt oxide content. Catalyst: 1 – Pd/Al_2O_3; 2 – Pd/0.1%Co/Al_2O_3; (3) Pd/0.3%Co/Al_2O_3; (4) Pd/0.4%Co/Al_2O_3; (5) Pd/0.3%Co/Al_2O_3 after ageing for 24 h at 650 °C; (6) Pd/0.3%Co/Al_2O_3 after ageing at 750 °C; (7) 0.3%Co/Al_2O_3; (8) Pd/5%Co_3O_4–Al_2O_3; (9) Pd/10%Co_3O_4–Al_2O_3; (10) Pd/15%Co_3O_4–Al_2O_3.

temperature exceeded 400 °C, the incorporation of Ni, Co or Fe oxides deteriorated the activity of 0.5%Pd/Al_2O_3.

The activity of the 0.3%Co/Al_2O_3 catalyst in methane combustion was low (87% conversion at 754 °C) (Fig. 4(a)). The catalysts prepared by depositing 0.5% Pd onto the Al_2O_3 surface covered with a cobalt oxide layer (0.5%Pd/*x*%Co/Al_2O_3) displayed a high activity, which depended on the amount of the cobalt oxide added (Fig. 4(a)). The catalytic activity of 0.5%Pd/0.3%Co/Al_2O_3 was higher than that of 0.5%Pd/Al_2O_3. When cobalt content was further increased to 0.4 wt.%, a decrease in catalytic activity was observed at temperatures higher than 400 °C (Fig. 4(a)). No CO was formed during CH_4 combustion over these catalysts. In the 0.5%Pd/*x*%Co/Al_2O_3 catalysts, the size of Pd crystallites increased with cobalt oxide content and Pd dispersion slightly decreased from 13.1% to 12% when cobalt oxide content was increased from 0.2% to 0.4% Co (Table 1). The size of Pd crystallites in these catalysts averaged from 8.6 nm to 9.9 nm. When crystallite size in the 0.5%Pd/0.3%Co/Al_2O_3 catalyst was measured by the XRD method, the crystallites of cobalt oxide were approximately 3.5 times the crystallites of PdO deposited onto its surface. We assume that the increase in the content of cobalt oxide is parallelled by the increase in the size of its crystallites, which accounts for the decrease in Pd dispersion in the catalysts. The measured SSA value of the Al_2O_3-washcoated support amounts to 8.9 m^2/g and is close to the calculated SSA value (10.1 m^2/g). The low SSA value is attributable to the high mass of the metallic monolithic support (21.5 g). Upon deposition of 0.5% Pd onto the cobalt oxide and the washcoat (Al_2O_3), the total SSA of the catalysts decreased, which is due to the increase in the size of the Pd crystallites on the surface of the catalysts (Table 1). In the 0.5%Pd/*x*%Co/Al_2O_3 catalysts Pd has been deposited onto the surface of the cobalt oxide covering the Al_2O_3 layer. In these catalysts the proportion of the cobalt oxide mass to the Al_2O_3 mass varied from 13 wt.% (0.5%Pd/0.2%Co/Al_2O_3) to 22.7 wt.% (0.5%Pd/0.4%Co/Al_2O_3), which is equivalent to the cobalt oxide loading in cobalt-containing catalysts for CH_4 combustion. In these catalysts, in the course of cobalt oxide deposition onto the Al_2O_3 surface, cobalt oxide at least partly deposited inside the pores of Al_2O_3 and thus reduced their volume, e.g. from 4 cm^3/g to 3.2 cm^3/g for the 0.5%/0.4%Co/Al_2O_3 catalyst. And this accounted for the decrease in the total SSA of the 0.5%/*x*%Co/Al_2O_3 catalysts (Table 1).

After 180 h of methane combustion over 0.5%Pd/0.3%Co/Al_2O_3, conversion dropped from 98.7% to 91.3% (at 558 °C). Tests on the thermal resistance of 0.5%Pd/0.3%Co/Al_2O_3 have shown that heating at 650 °C for 24 h fails to reduce catalytic activity at 560 °C (conversion 98.4%). The rise in heating temperature to 750 °C reduced conversion to 81.6% at 553 °C (Fig. 4(a)). Heating at 1000 °C for 24 h notably decreased catalytic activity (41.7% conversion at 554 °C) owing to the reduction of PdO to metallic Pd and to the agglomeration of Pd particles on the catalyst surface (XPS).

The increase in Pd load from 0.5% to 1% in the Pd/Al_2O_3 catalyst is parallelled by a considerable decrease in the SSA of the catalyst and in Pd dispersion (the size of Pd crystallites increases) (Table 1), and catalyst activity decreases. The decrease in Pd dispersion with the increase in Pd content has also been reported by other researchers [14]. They observed, for example, that when Pd content increased from 0.4% to 2.12%, Pd dispersion decreased from 5% to 1.5%. The addition of 0.3% Co to 1%Pd/Al_2O_3 catalyst raises its activity (Fig. 5) due to the rise in Pd dispersion (from 3.8% to 20.3%) and to the decrease in Pd crystallite size (from 29.6 nm to 5.5 nm). The considerable rise in Pd dispersion in the catalyst where 1% Pd has been deposited onto the cobalt oxide layer seems to be attributable to the strong interaction between Pd and cobalt oxide on the catalyst surface. This interaction are stronger than the interaction between Pd and Al_2O_3. These strong interactions reduce the surface mobilitity of Pd, which prevents the agglomeration of Pd crystallites, thus contributing to the rise in Pd dispersion. A similar, noticeable rise in Pd dispersion has been observed by Guczi et al. [15] with sol–gel silica supported 5 wt.%Pd–Co catalysts containing different amounts of Co. In this catalysts, Pd dispersion measured by the XRD method increased from 7.8% (0% Co) to 16% (33% Co).

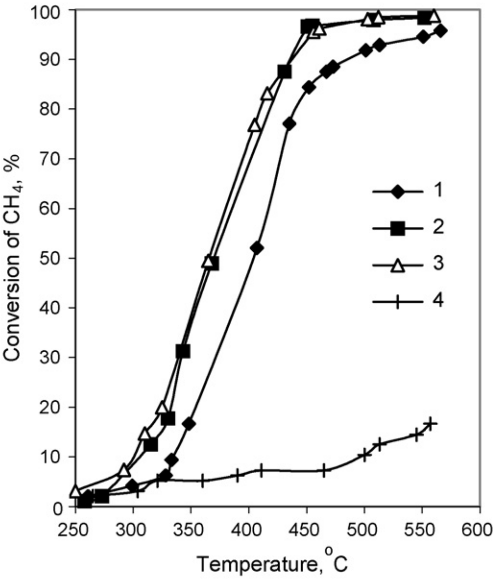

Fig. 5. Comparison of methane conversion over monolithic catalysts. (1) Fresh 1%Pd/Al_2O_3; (2) fresh 1%Pd/0.3%Co/Al_2O_3; (3) 1%Pd/0.3%Co/Al_2O_3 after 20 h on stream; (4) 1%Pd/0.3%Co/Al_2O_3 after ageing for 24 h at 1000 °C.

The application of a mixed washcoat, 95%Al_2O_3–5%Co_3O_4, to Pd-based catalysts increases the activity of the 0.5%Pd/Al_2O_3 catalyst (Fig. 4(b)) since the SSA value of the 5%Co_3O_4–95%Al_2O_3 washcoat exceeds that of Al_2O_3 (370 m^2/g and 349 m^2/g, respectively). On the surface of fresh 0.5%Pd/5%Co_3O_4–95%Al_2O_3, palladium occurs mainly in the form of PdO and displays a notable mobility under variable temperature conditions, undergoing reduction and oxidation in a cyclic mode. Also cobalt underwent cyclic reduction and oxidation: from Co^{+2} at room temperature to the dominant form of Co^0 at 500 °C (in the UHV XPS chamber). The addition of 10% cobalt oxide into the washcoat failed to enhance the activity of 0.5%Pd/Al_2O_3 despite a slight decrease in the SSA of the washcoat (Table 1). The increase in cobalt oxide content to 15 wt.% decreased the activity of the catalyst in response to a considerable reduction in the SSA of the washcoat (from 349 m^2/g to 312 m^2/g).

4. Conclusions

The deposition of Ni, Co, Ce or Fe oxides onto the washcoat surface in 0.5%Pd/Al_2O_3 enhances the conversion of methane. When Pd is deposited onto the surface of the cobalt oxide covering Al_2O_3 (Pd/0.3%Co/Al_2O_3 catalyst) or onto the surface of the mixed washcoat (5%Co_3O_4–Al_2O_3), the activities of these catalysts are higher than that of 0.5%Pd/Al_2O_3. When the cobalt oxide content in the catalyst is further increased, catalytic activity decreases. The highest activities were those of the 0.5%Pd/0.3%Co/Al_2O_3, 1%Pd/0.3%Co/Al_2O_3 and 0.5%Pd/5%Co_3O_4–Al_2O_3 catalysts. Total SSA, Pd dispersion and average size of the Pd crystallites in the catalysts tested depend both on the load of

Pd in the catalyst and on the composition of the washcoat onto which palladium was deposited. In the x%Pd/y%Co/Al_2O_3 catalysts, they also depend on the cobalt oxide content. The incorporation of 0.3% Co into the 1%Pd/Al_2O_3 catalyst notably raised Pd dispersion (from 3.8% to 20.3%) and reduced the average size of Pd crystallites (from 29.6 nm to 5.5 nm), thus enhancing its activity. The increase in the Pd amount of the catalyst (from 0.5% to 1%), as well as the increase in the cobalt oxide quantity (from 0.2% to 0.4%), reduces the SSA from 8.9 m^2/g (Al_2O_3/support) to 2.9–5.2 m^2/g (x%Pd/y%Co/Al_2O_3/support). The SSA of the washcoat powders increases upon the incorporation of 5 wt.% Co_3O_4 (from 349 m^2/g to 370 m^2/g). In these catalysts Pd and Co occurred in the form of PdO and the $CoAl_2O_4$ spinel, respectively (XPS). At increased temperature, under reducible UHV conditions, PdO and Co^{+2} were reduced at 200 °C and above 300 °C, respectively. At 500 °C, in vacuo, Pd agglomerated irreversibly in the form of metallic crystallites. Under the same conditions, the reduction in cobalt was reversible.

Acknowledgement

The study was financed from the 2005–2008 Scientific Research Funds under Project No 3T09B 121 29.

References

[1] P. Gelin, M. Primet, Appl. Catal. B 39 (2002) 1.
[2] H. Arai, M. Machida, Catal. Today 10 (1991) 81.
[3] H. Arai, H. Fukuzawa, Catal. Today 26 (1995) 217.
[4] L. Wachowski, P. Kirszensztejn, R. Łopatka, Mater. Chem. Phys. 37 (1994) 29.
[5] S. Suhonen, M. Valden, M. Pessa, Appl. Catal. A 207 (2001) 113.
[6] K. Eguchi, H. Arai, Appl. Catal. A 222 (2001) 359.
[7] H. Widjaja, K. Sekizawa, K. Eguchi, H. Arai, Catal. Today 47 (1999) 95.
[8] H. Widjaja, K. Sekizawa, K. Eguchi, H. Arai, Catal. Today 35 (1997) 197.
[9] E. Garbowski, M. Guenin, M. Marion, M. Primet, Appl. Catal. 64 (1990) 209.
[10] S. Miao, Y. Deng, Appl. Catal. B 31 (2001) 91.
[11] A. Frydman, D.G. Castner, M. Schmal, C.T. Campbel, J. Catal. 152 (1995) 164.
[12] P. Arnoldy, J.A. Moulijn, J. Catal. 93 (1985) 38.
[13] L. Guczi, Z. Schay, G. Stefler, F. Mizukami, J. Mol. Catal. A 141 (1999) 177.
[14] L.S. Escandon, S. Ordonez, A. Vega, F.V. Diez, Chemosphere 58 (2005) 9.
[15] L. Guczi, L. Borko, Z. Schay, D. Bazin, F. Mizukami, Catal. Today 65 (2001) 51–57.