

Promoted cobalt oxide catalyst on the metallic structured reactor filling for VOC combustion as an alternative to noble metal catalysts

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VOC combustion is a demanding process for both the reactor and the catalyst design. As we have proved in recent papers the diffusional limitation of reaction rate that occurs during combustion may be overcome by designing the metallic microstructures used as reactor internals. Their application on an industrial scale depends on the development of an efficient method of catalyst layering on metallic supports and the optimisation of a fine catalyst structure which would not change the elaborated microstructure geometry. In this study we propose the Langmuir-Blodgett (LB) film method to deposit various metals (Al, Co) in the form of catalyst organic precursors. The film forming abilities of the precursors were checked by surface pressure measurements upon film compression, Brewster Angle Microscopy and by the monolayers stability measurements. The amount of the deposited materials was controlled by the LB parameters and verified by the TG measurements. The catalyst obtained in this way were characterized at various stages of the preparation by SEM/XFS, XPS, AFM and RM methods and tested in n-hexane combustion. Oxidation of the Al washcoat precursor led to the formation of γ - Al_2O_3 improving the properties of the Al_2O_3 layer (α phase) developed on the pre-calcined CrAl carrier. Oxidation of cobalt stearate deposited on the CrAl produced dispersed Co_3O_4 spinel. The cobalt catalysts were active in combustion showing resistance to sintering. Compared to standard Pt supported catalyst it demonstrated twice as low activation energy (50 kJ/mol).

Keywords: Langmuir-Blodgett technique, structured carrier, wash-coat layer, Raman microscopy, XPS quantitative analysis.

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INTRODUCTION

There is no doubt that a world-wide standard for the reduction of the emission of exhaust gases from vehicle engines are ceramic monoliths with three-way catalysts based on noble metals. Nevertheless, volatile organic compounds (VOCs) and particulate matter emission still pose a vital environmental problem, receiving a lot of attention in the literature. The main sources of VOC are road transport, power stations, chemical industry utilizing solvents, oil industry and agriculture. In fact, by high dilution, a huge flow rate of gas streams, the risk of carbon deposits, the removal of VOC from atmosphere pose a new challenge for both engineers and chemists. Our approach is thus based on the application of microstructural filling of reactors, whose idea is described in an accompanying paper dealing with engineering aspects of the reactor structures¹.

An intrinsic problem connected with the utilization of metallic structural carriers is finding a sufficient method of catalyst depositing on metallic surface. Not only should the deposited catalyst material (washcoat and catalyst) adhere to the surface, but also should leave an elaborate duct shape unchanged¹. The problem lays in achieving a thin and uniform catalyst layer of a dimension comparable to a channel diameter, and preferably, of a controlled structure. Commonly used depositing methods (deposition from suspension, sole-gel) are not able to fulfill all these requirements and especially to control the amount of the deposited material.

In this paper which follows a series of papers on the same problem²⁻⁵ we present the cobalt spinel catalyst promoted with noble metals (Pd/Pt) which is considered as a possible alternative to noble metal catalysts. In our previous paper^{4,5} we described the Langmuir-Blodgett technique which was used to deposit metal containing material onto the pre-calcined surface of chromium-aluminium steel and in this way to obtain model well-defined materials to survey catalyst structure-activity relationship. Here we focus on the properties of bimetallic catalytic systems containing Co and Co/Pd and Co/Pt, respectively. According to recent findings, among other oxides of spinel, corundum or perovskite structure^{6,7} cobalt spinel appears very promising for VOCs combustion. It shows low temperature of combustion of VOCs oxygenates⁶ and soot particles⁸⁻¹⁰. These two latter ones cannot be easily oxidised using noble metals alone^{8,11}. However, cobalt spinel used in combination with noble metals is hoped to produce flexible catalysts prepared for various kinds of reactions that occur during VOCs combustion and even NO_x reduction¹²⁻¹⁶.

EXPERIMENTAL

Stainless chromium-aluminium steel leaves (steel 00H20J5 – 0.3 mm thick, Baildon, Poland); denoted here as CrAl, were used as the structural units described in an accompanying paper¹ and as the catalyst carriers in this part of the study. The steel is similar to kanthal alloy and it contains: Cr – 20.37%, Al – 5.17% (and also Mn – 0.25%, Ni – 0.16%, Cu – 0.034%, Co – 0.021%). As a

reference carrier Co foil (+99.99%, 0.1 mm, Aldrich) was also used.

The catalyst preparation consisted of the following steps:

- Carrier pre-treatment: calcination of an initial CrAl steel samples in air at 1000°C for 24 h.
- Material deposition: layering Al and Co organic compounds on pre-calcined samples by LB technique^{4, 5}.
- Catalyst promotion: chemisorption of Pt or Pd nitrates (of a formulae: $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$, respectively) on the surface deposited with cobalt oxide.
- Catalyst activation: oxidation of the deposited samples in air at 800°C for 2 h.

The promoters were deposited onto the catalyst surface via chemisorption from 0.001 M $\text{Pd}(\text{NO}_3)_2$ and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solutions (water + 10 vol % glycerine). The samples immersed in a solution were heated to 90°C for 1 h and then dried and calcined at 800°C for 2 h.

The surface of the samples was examined by scanning electron and atomic force microscopy (SEM/EDX, AFM) and photoelectron spectroscopy (XPS).

SEM images were obtained in Philips XL 20 microscope equipped with EDX microprobe.

XPS analyses were carried out in a VG Scientific ESCA-3 photoelectron spectrometer using AlK α radiation 1486.6 eV from X-ray source operating at 13 kV and 10 mA. Working pressure was lower than $5 \cdot 10^{-7}$ Pa. All spectra were recorded at a photoelectron take-off angle of 45°. Binding energies were corrected to the C 1s peak from the surface carbon at 284.8 eV. The spectra were preprocessed by Shirley's background and K α band removal. The composite bands were found by fitting single peaks, doublets or multiplets, and finally, to find their maxima positions, they were decomposed into symmetric Gaussian-Lorentzian peaks. The procedure was aided by the spectra database collected for the model compounds of elements used in this study. The spectra were measured in the region of C 1s, O 1s, Mg 1s, Al 2p, Cr 2p, Fe 2p, Co 2p, Pd 3d and Pt 4f. The measured values of binding energies (BE) are generally in keeping with the reference data found in NIST database. Mol fractions of the elements present on the surface were calculated according to the formula given in¹².

AFM ex situ images have been obtained using Nanoscope E (Digital Instruments, DI, California) working in the contact mode using the standard silicon nitride cantilevers with the spring constant of 0.12 N/m. The AFM image analysis was carried out using DI software procedures to determine surface roughness that is represented by RMS parameter. More details concerning the measurement procedure can be found elsewhere¹³.

Catalytic tests were performed in a microreactor unit operated at a continuous flow of reactants at atmospheric pressure. A small glass tube reactor, 4.25 mm ID, was placed inside a thermostat. A bed filling the reactor was composed of several pieces of a CrAl leaf with the active catalyst deposited. The geometrical surface area of the carrier was approximately 1 cm² and the height of the bed was around 5 mm. The reaction mixture contained 20 mol % O₂, 0.39 mol% of n-hexane vapour and the balance of helium. A controlled amount of n-hexane vapour was supplied to the reaction mixture from a saturator stabilised at a selected temperature. The n-hexane partial pressure at a given temperature was calculated from the

Antoine's equation. The reaction proceeded at a total flow rate 103 ml/min and in the temperature range from 100 – 900°C. The products were analysed using a gas chromatograph (SRI Instruments, 8610C) equipped with TCD detector and the system of two columns packed with Carboxen 1004 and HaysepQ (2m x 1/16", Supelco).

To obtain temperature dependence of the reaction rate, n-hexane oxidation was initiated at 100°C and after several GC analyses the temperature was increased by 20°C until CO₂ appeared as a reaction product, since then, the temperature was increased by 10°C and 3 GC analyses were performed at each temperature. Each point on kinetic curves is a mean value of reaction rate at a given temperature.

RESULTS AND DISCUSSION

It has been demonstrated in^{2, 4, 5} that pre-calcination leads to the segregation of Al₂O₃ layer containing traces of Fe₂O₃ (also FeOHO), Cr₂O₃ and Mg(OH)₂ as measured by XPS (Fig. 1). The layer is around 2 μm thick and partly of corundum structure². On the surface spotted with EDX mapping, neither Co₃O₄ nor Pd or Pt is visible on the surface, evidencing high dispersion of the metals introduced.

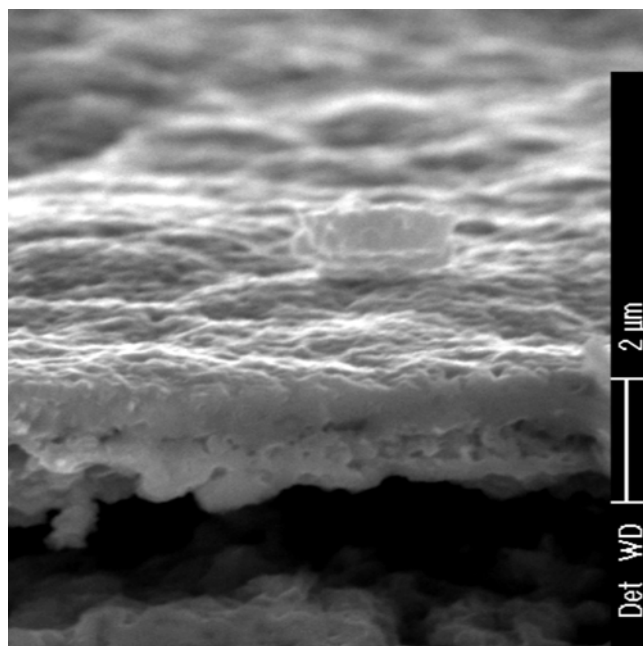


Figure 1. Cross-section of the pre-calcined carrier in SEM (5000x)

There is a great difference between palladium and platinum promoted catalysts both in the oxidation state and surface structure, which was observed using XPS and AFM methods. On the Pd promoted catalysts, the band recorded at 336.5 eV, one of the bands in doublets from Pd 3d electrons, can be attributed to PdO. A small contribution also comes from the band at 338.6 eV, which may arise from a palladium complex coordinated either by N or O atoms coming from residual only partly decomposed palladium nitrate¹⁹. With reference to Pt promoted catalyst, the band at 70.9 eV, again one of the bands in the expected doublet (7/2 and 5/2) from Pt 4f electrons, was assigned to metallic Pt¹⁴.

As regards quantitative analysis of XPS results the cobalt oxide content (Table 1), decreases slightly with the

Table 1. Surface composition of the cobalt catalysts according to LB and XPS

Sample name	Composition of the surface oxide layer from LB (mol fraction)	Surface composition from XPS (mol fraction)					
		CoO**	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	PdO	Pt
CrAl	–	–	0.613	0.048	0.028	–	–
0.1Co/CrAl	$4.2 \cdot 10^{-4}$	0.020	0.859	0.061	0.059	–	–
0.3Co/CrAl	$1.2 \cdot 10^{-3}$	0.052	0.768	0.104	0.075	–	–
0.7Co/CrAl	$2.9 \cdot 10^{-3}$	0.013	0.871	0.064	0.053	–	–
Pd+0.3Co/CrAl	$1.2 \cdot 10^{-3}$	0.018	0.049	0.039	0.052	0.841	–
Pd+0.7Co/CrAl	$2.9 \cdot 10^{-3}$	0.011	0.021	0.031	0.023	0.914	–
Pt+0.3Co/CrAl	$1.2 \cdot 10^{-3}$	0.050	0.717	0.123	0.087	–	0.022

* values derived from LB transfer parameters and related to total amount of Al₂O₃ [2]

** according to XPS BE of Co 2p can be ascribed to CoO rather than to Co₃O₄ which was accounted for the thermal decomposition of Co₃O₄ under high vacuum conditions [2]

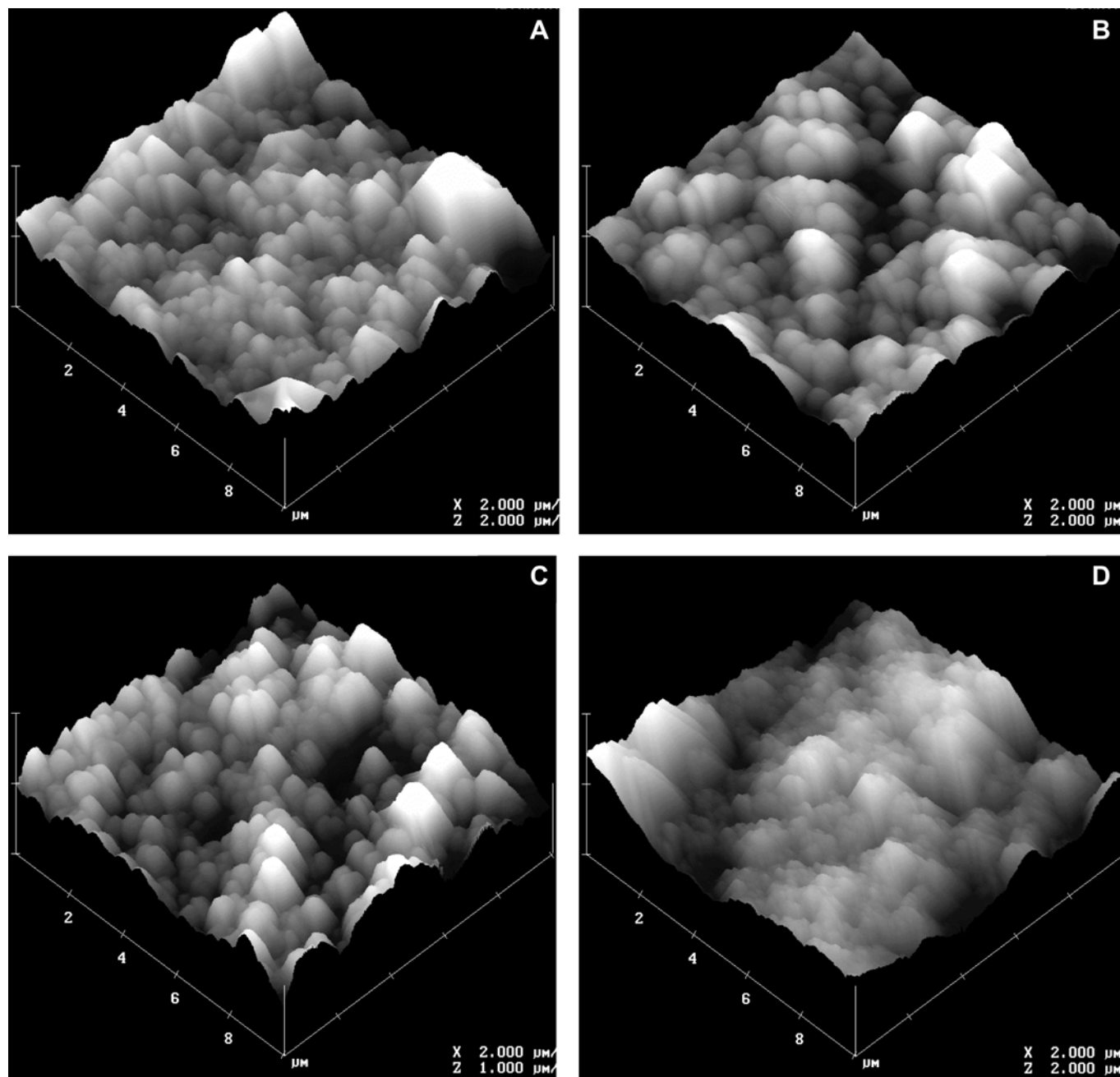


Figure 2. AFM images of the catalysts at various stages of the preparation (10x1- μm): A – pre-calcined CrAl sample, B – 0.7Co/CrAl sample, C – Pd+0.7Co/CrAl sample, D – Pt+0.7Co/CrAl sample

sample loading with Co, however, the amount of cobalt is on the low side reaching the lower limit of the analysis sensitivity. Taking into account that photoelectrons come from a very superficial region, this result may also imply reduced dispersion of cobalt oxide on the 0.7Co/CrAl

sample. The surface coverage changes upon chemisorption of Pd, which, judging from the value of the molar fraction, coats the surface almost totally. As it can be inferred from the changes in concentration of other oxides, PdO presumably locates more on alumina surface rather than on

Table 2. Surface parameters derived from AFM and XPS results. SEC – CoO surface enrichment coefficient, RMF – roughness coefficient, SA – relative surface area related to geometrical area

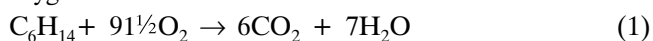
Sample name	SEC from XPS	RMS from AFM (nm)	SA from AFM
CrAl	–	235	1.36
0.1Co/CrAl	16	–	–
0.3Co/CrAl	15	–	–
0.7Co/CrAl	1.5	199	1.25
Pd+0.3Co/CrAl	15	–	–
Pd+0.7Co/CrAl	10	303	1.31
Pt+0.7Co/CrAl	4.2	155	1.21

* for fitting Arrhenius equation

cobalt oxide surface. Let us also note that the surface content of the Pd+0.7Co/CrAl sample is higher than that of the Pd+0.3Co/CrAl, which further reflects on their catalytic activity. The important though not very much evidenced observation may be that the Pt content on the surface of the Pt+0.3Co/CrAl sample is on the lowest side, possibly indicating diffusion of Pt through the Al₂O₃ matrix. The change of the chemical environment of the Pt crystallites is supportive of the relatively low value of the binding energy of Pt⁰ (70.9 eV) found on this sample as compared to the value of metallic Pt found in the XPS database (71.0 or 71.1 eV). It is also possible that in this case chemisorption of platinum nitrate did not take place with a satisfactory efficiency, but this needs more experiments to be performed.

AFM analysis is one of the few methods for the determination of the surface area of the samples deposited on metallic carriers. (Figure 2). In this study we have mainly focused on ascertaining the surface roughness (RMS) and relative surface area (SA) of the samples (Table 2). The SA values were related to the geometric area of the images (10x10 μm). Upon depositing Co₃O₄ on the surface, both the RMS and SA values decrease. The highest RMS value of 303 nm was recorded for the Pd promoted sample with SA comparable to the initial calcined CrAl sample. Conversely, the lowest values of both RMS and SA were recorded for Pt promoted catalysts. The surface enrichment coefficient (SEC) is a ratio between the content of a specific cobalt oxide calculated from XPS (Table 1) and the one calculated from LB (Table 1). These values are comparable for the 0.1 and 0.3Co/CrAl samples and amount to about 15. The decreased value of SEC of Pd+0.7Co/CrAl in comparison with 0.7Co/CrAl sample implies that Pd partly covers cobalt oxide crystallites. The decreased values of RMS and SA parameters and increased value of SEC of Pt+0.7Co/CrAl, comparing to their counterparts, may suggest that Pt is situated in Al₂O₃ pores, which may explain why it did not show a promoting effect in catalytic tests.

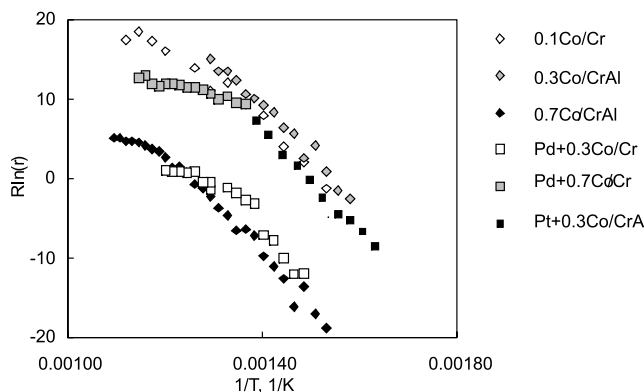
The results of the kinetic tests of the series the cobalt catalysts of various loading (0.1Co/CrAl, 0.3Co/CrAl, 0.7Co/CrAl) and composition (promoted with Pt and Pd) are presented in Figure 3 and in Table 3. These were prepared according to the following kinetic approach. Oxidation of n-hexane (C6) performed in the excess of oxygen:



can be simplified into a simple reaction pattern described by a first-order kinetic equation:

Table 3. Kinetic parameters evaluated from Arrhenius plots.

Sample name	Temp. range ^a (°C)	E _{app} (kJ/mol)
0.1Co/CrAl	380 – 520	51
0.3Co/CrAl	360 – 500	60
0.7Co/CrAl	350 – 550	56
Pd+0.3Co/CrAl	380 – 460 470 – 640	54 16
Pd+0.7Co/CrAl	415 – 590	17
Pt+0.3Co/CrAl	340 – 450	66

**Figure 3.** Arrhenius plots for the catalysts tested in n-hexane combustion. Description according to Table 3

$$r = k \cdot c_{\text{C6}} = A_{\text{app}} \exp\left(\frac{-E_{\text{app}}}{RT}\right) \cdot c_{\text{C6}} \quad \frac{\text{mol C6}}{\text{mol cat.} \cdot \text{s}} \quad (2)$$

where, *r* is a specific reaction rate, *k* – rate constant, *c*_{C6} – n-hexane concentration in the gas phase, *A*_{app} – a pre-exponential factor and *E*_{app} – activation energy. The specific reaction rate, *r*, expressed in equation (2) corresponds to turn-over frequency (TOF, 1/s), if the catalyst amount is equal to the total number of active centres. This is in fact the considered case of the low surface concentration of the highly dispersed Co₃O₄ catalyst.

Approximating the test reactor to a plug flow differential reactor (*c*_{C6} approximately constant), the kinetic equation can be expressed as follows:

$$r \cong A_{\text{app}} \exp\left(\frac{-E_{\text{app}}}{RT}\right) \quad (1/\text{s}) \quad (3)$$

which has been used to obtain Arrhenius plots presented in Figure 3. Thus also, the reaction rate was calculated directly from the C6 conversion.

The apparent kinetics derived from these experiments can be used for a rough evaluation of the catalytic performance and of the optimised reactor structures. The values of activation energy (Fig. 3), the general trend is common for all unpromoted cobalt catalysts with an average value amounting to 56 ± 3 kJ/mol. An addition of a small amount of Pd changes the activity of the cobalt catalysts, which is reflected by a significant decrease in the value of apparent activation energy but estimated in the slightly higher temperature range. No such effect was observed for the Pt-promoted sample, which did not differ in activation energy from the unpromoted samples.

Eventually, the cobalt catalysts regardless of their composition and loading were able to initiate the reaction at around 300°C. A similar temperature of combustion initiation was observed for propane¹⁰, for soot¹⁵ and for methane¹⁶. However, the temperature of the reaction initiation measured by us should be derived from real kinetics which would be free from diffusional limitations.

In the light of the gathered results, we may assume that active centres of combustion should constitute small cobalt oxide spinel-type crystallites, highly dispersed in the alumina matrix. Including both Co^{+2} in tetrahedral and Co^{+3} in octahedral positions, cobalt spinel seems a good candidate to enhance electron transfer in the catalytic combustion cycle. Thus Co^{+2} located at a relatively opened coordination position can be a centre of oxygen adsorption and formation of active oxygen species which are a prerequisite for catalytic oxidation. Palladium oxide seems a reaction initiator as it has also been suggested in¹⁰ providing another type of active centres for oxygen adsorption, it reduces activation energy of the overall process introducing another more efficient path into the reaction network.

CONCLUSIONS

The prepared cobalt catalysts tested in combustion of n-hexane, occurred relatively active in the combustion of n-hexane as compared to the commercial $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst; despite higher temperature of the reaction initiation (ca. 330°C), they had almost twice as low activation energy (approximately 52 kJ/mol) and could operate at much higher temperatures. An addition of the Pd promoter to the cobalt catalyst gave rise to the decrease in the activation energy to around 15 kJ/mol. No activation effect was noted for the Pt containing catalysts. The activity changes due to promoters addition were correlated to the changes of surface composition and dispersion of the catalysts. The kinetic results obtained in a tubular test reactor can only be treated qualitatively for the preliminary catalyst evaluation since they are strongly affected by the diffusional effects. For further modelling studies gradientless reactor should be applied.

Acknowledgements

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LITERATURE CITED

- (1) Kołodziej A., Łojewska J., Kleszcz T.: „Structured catalytic reactor for VOC combustion”, submitted to Polish Journal of Chemical Technology.
- (2) Kołodziej A., Łojewska J.: *Catal. Today* **2005**, 105, 378.
- (3) Łojewska J., Kołodziej A., Dynarowicz-Łątka P., Wesełucha-Birczyńska A.: *Catal. Today* **2005**, 101, 81.
- (4) Łojewska J., Dynarowicz-Łątka P., Kołodziej A.: *Thin Solid Films* **2006**, 495, 299.
- (5) Łojewska J., Kołodziej Żak J., Stoch J.: *Catal. Today* **2005**, 105, 655.
- (6) Busca G., Daturi M., Finocchio E., Lorenzelli V., Ramis G., Willey R. J.: *Catal. Today* **1997**, 33, 239.
- (7) Marchetti L., Forni L.: *Appl. Catal. B: Environmental* **1998**, 15, 179.
- (8) Neeft J. P. A., Makkee M., Moulijn J. A.: *Appl. Catal. B: Environmental* **1996**, 8, 57.
- (9) Neeft J. P. A., van Pruissen O. P. P., Makkee M., Moulijn J. A.: *Appl. Catal. B: Environmental*, **1997**, 12, 21.

- (10) Harrison P. G., Ball I. K., Daniell W., Lukinskas P., Céspedes M., Miró E. E., Ulla M. A., *Chem. Eng. J.* **2003**, 95, 47.
- (11) Ahlström-Silversand A. F., Odenbrand C. U. I.: *Chemical Engineering Journal* **1999**, 73, 205.
- (12) Wojciechowska M., Haber J., Łomnicki S., Stoch J.: *J. Mol. Catal. A: Chemical* **1999**, 141, 155.
- (13) Zak J., Kolodziej-Sadlok M.: *Electrochim. Acta* **2000**, 45, 2803.
- (14) NIST database: <http://webbook.nist.gov/chemistry/>, LaSurface database <http://www.lasurface.com/>
- (15) Skonglundh M., Johansson H., Löwendahl L., Jansson K., Dahl L., Hirschauer B.: *Appl. Catal. B: Environmental* **1996**, 7, 299.
- (16) Xiao T., Ji S., Wang H., Coleman K. S., Green M. L. H.: *J. Mol. Catal. A: Chemical* **2001**, 175, 111.