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Pd/Pt promoted Co_3O_4 catalysts for VOCs combustion Preparation of active catalyst on metallic carrier

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Abstract

Emission control of volatile organic compounds (VOCs) is one of the priorities for environmental catalysis. Metallic microstructural short-channel reactors of various geometries are regarded as an alternative to ceramic monoliths. The paper presents the results on the catalyst preparation and optimisation. Chromium-aluminium (CrAl) steel was surveyed in terms of its applicability for carrier manufacturing and catalyst depositing. Alumina washcoat and cobalt catalyst were deposited as organic precursors using Langmuir–Blodgett method (LB) onto precalcined CrAl sheets. Additional noble metal promoters (Pd and Pt) were deposited by chemisorption. The LB method occurred useful for the preparation of nanocomposite catalyst since it enabled controlling the quantity and even distribution of the deposited material. The catalyst surface at various stages of preparation was examined using SEM, XPS and AFM methods. Catalytic tests showed that small amount of Co_3O_4 spinel, highly dispersed on Al_2O_3 layer, is active in combustion of diluted *n*-hexane. The apparent activation energy for the obtained cobalt catalyst (about 52 kJ/mol) was twice as low as for a standard Pt/Al_2O_3 catalyst. The promoting effect observed for Pd-containing cobalt catalysts by the decrease in the activation energy to around 15 kJ/mol, was correlated to the high surface concentration and dispersion of the cobalt catalyst containing PdO.

Keywords: VOCs combustion; Catalyst deposition method; Langmuir–Blodgett technique; Cobalt catalyst; Pd/Pt promoters

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1. Introduction

While the emission of exhaust gases from vehicle engines has been successfully reduced by introducing ceramic monoliths with three-way catalysts, which for last two decades has become a world-wide standard, volatile organic compounds (VOCs) and particulate matter pose still a vital environmental problem. The strategy for this should involve high intensification of mass and heat transport phenomena, since combustion of VOCs, usually diluted in an end-pipe gas stream, is limited by diffusional processes. Our approach is thus based on the application of microstructural internals of reactors, whose idea is described in an accompanying paper dealing with engineering aspects of the reactor structures [1].

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 unchanged [1]. 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, sol–gel) are not able to fulfil all these requirements and especially to control the amount of the deposited material.

To meet the challenge the Langmuir–Blodgett (LB) technique was used to deposit cobalt catalyst onto the

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surface of precalcined chromium-aluminium steel. The LB technique gives the opportunity to control several physical parameters of layers transferred such as molecular packing, lateral pressure, composition and finally deposited material quantity [2,3]. Thus, it appears extremely suitable at the stage of the optimisation of catalyst structure.

In an attempt to find an active catalyst of VOCs combustion which would be able to initiate the reaction at low temperatures and which would be temperature resistant, we tested mono- and bimetallic catalytic systems containing Co and Co/Pd, Co/Pt, respectively. According to recent findings, among other oxides of spinel, corundum or perovskite structure [4,5], cobalt spinel appears very promising for VOCs combustion. It shows low temperature of combustion of VOCs oxygenates [4] and soot particles [6–8]. These two latter cannot be easily oxidised using noble metals alone [6,9]. 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 reduction [10–14].

An ultimate aim of the study undertaken by us is to work out an efficient method of catalyst layering onto the metallic surface and preparing an active catalyst for VOCs combustion. Particular objective of this work is to examine the influence of Pd and Pt promoters on the cobalt catalyst activity.

2. Experimental

Stainless chromium-aluminium steel leaves (steel 00*H*20*J*5—0.3 mm thick, Baildon, Poland); denoted here as CrAl, were used as the structural units described in an accompanying paper [1] 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 precalcined samples by LB technique.
- *Catalyst promotion*: chemisorption of Pt or Pd nitrates (of a formulae: $Pt(NH_3)_4(NO_3)_2$ and $Pd(NO_3)_2$, respectively) on the surface deposited with cobalt oxide.
- *Catalyst activation*: oxidation of the deposited samples in air at 800 °C for 2 h.

For LB depositing, we used aluminium(III) 9-octadecenylacetoacetate diisopropoxide (AKA, $C_{28}H_{53}AlO_5$, 90%, *Gelest*) and cobalt stearate ($Co(C_{18}H_{35}O_2)_2$) as a washcoat and catalyst precursors, respectively. AKA is applied on industrial scale to improve dispersion of magnetic powders by SONY corporation. Cobalt stearate was, in turn, obtained for the purpose of this research by in situ precipitation in the Langmuir trough from $Co(NO_3)_2$ (99.999, Aldrich, 0.001 M aqueous solution) and stearic acid (SA, 99+, Aldrich). The details concerning LB transfer conditions are described in our previous papers [15,16]. All in all, being able to introduce multilayers of homogeneous film onto the solid surface, the LB method gives the opportunity to control the amount and dispersion of the deposited material. The amounts of Co_3O_4 introduced onto the surface and calculated from LB transfer parameters are presented in Table 1.

The promoters were deposited onto the catalyst surface via chemisorption from 0.001 M $Pd(NO)_3$ and $Pt(NH_3)_4(NO_3)_2$ 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 Al Kα radiation 1486.6 eV from X-ray source operating at 13 kV and 10 mA. Working pressure was lower than 5×10^{-7} Pa. All spectra were recorded at a photoelectron take-off angle of 45°. Binding energies (BE) were corrected to the C 1s peak from the surface carbon at 284.8 eV. The spectra were preprocessed by Shirley's background and Kα 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 are generally in keeping with the reference data found in NIST

Table 1
Preparation of cobalt catalysts, Co_3O_4 content in Al_2O_3 matrix calculated from LB transfer parameters [15]

Sample name	Preparation method	Catalyst content	
		wt.%[a]	mol fraction[a]
Co_3O_4			
0.1 Co/CrAl	LB: 10 layers CoSA	0.10	4.2×10^{-4}
0.3 Co/CrAl	LB: 43 layers CoSA	0.30	1.2×10^{-3}
0.7 Co/CrAl	LB: 100 layers CoSA	0.69	2.9×10^{-3}
Co foil	Precalcined Co foil	–	–
Pd + 0.3 Co/CrAl	+Pd chemisorption	0.30	4.2×10^{-4}
Pd + 0.7 Co/CrAl	+Pd chemisorption	0.69	1.2×10^{-3}
Pt + 0.3 Co/CrAl	+Pt chemisorption	0.30	2.9×10^{-3}
Pt			
0.3 Pt/Al_2O_3	Commercial Pt catalyst	0.35 (Pt wt.%)	4.9×10^{-4}

[a] Fractions related to the amount of Al_2O_3 formed on the surface after calcination of CrAl.

database. Mol fractions of the elements present on the surface were calculated according to the formula given in [17].

The AFM ex situ images were 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 elsewhere [18].

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 i.d., 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 cm^2 and the height of the bed was around 5 mm. The reaction mixture contained 20 mol% O_2, 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 to 900 °C. The products were analysed using a gas chromatograph (SRI Instruments, 8610*C*) equipped with TCD detector and the system of two columns packed with *Carboxen* 1004 and *HayesepQ* (2 m × 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 CO_2 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.

3. Results and discussion

The SEM images of the surface of the precalcined CrAl and precalcined Co foil are presented in Fig. 1. Precalcination of CrAl leads to the segregation of Al_2O_3 layer containing traces of Fe_2O_3 (also FeOHO), Cr_2O_3 and

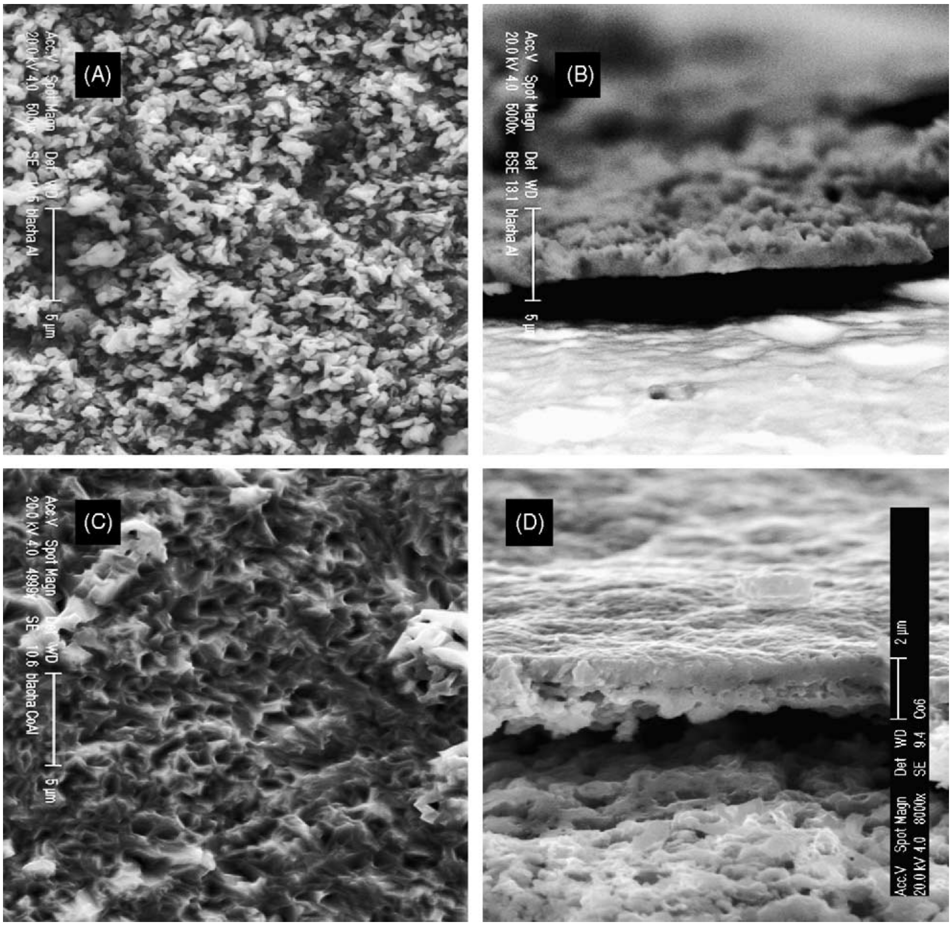

Fig. 1. SEM images of the precalcined samples of metallic carriers for cobalt catalysts: (A) CrAl (5000×); (B) a cross section of the same CrAl sample (5000×); (C) Co foil (5000×); (D) a cross section of the same Co sample (7500×).

Table 2
Surface composition of the cobalt catalysts according to XPS

Sample name	Surface composition from XPS (mol fraction)					
	CoO	Al_2O_3	Fe_2O_3	Cr_2O_3	PdO	Pt
CrAl	–	0.613	0.048	0.028	–	–
0.1 Co/CrAl	0.020	0.859	0.061	0.059	–	–
0.3 Co/CrAl	0.052	0.768	0.104	0.075	–	–
0.7 Co/CrAl	0.013	0.871	0.064	0.053	–	–
Pd + 0.3 Co/CrAl	0.018	0.049	0.039	0.052	0.841	–
Pd + 0.7 Co/CrAl	0.011	0.021	0.031	0.023	0.914	–
Pt + 0.3 Co/CrAl	0.050	0.717	0.123	0.087	–	0.022

$Mg(OH)_2$ as measured by XPS (Fig. 1 A and B). The layer is around 2 μm thick and partly of corundum structure [15]. Depositing the Al precursor and its further oxidation gives washcoat built of γ-Al_2O_3 and depositing the Co precursor—the catalyst in form of the dispersed spinel structure, as evidenced by XPS and Raman spectroscopy [15]. For comparison also the surface of precalcined Co foil, used further as a reference sample for the catalytic tests, is presented in Fig. 1C and D. Cobalt oxide layer grown on the metallic bulk is around 2 μm thick and built of Co_3O_4 spinel [15,19]. What these two carriers have in common is the oxide matrix in form of dispersed alumina or cobalt oxide layer which can be treated as a support for active centres of combustion.

In an attempt to assign oxidation states and molar content of metals present on the samples surface, XPS analyses were performed. The binding energies of the studied elements were linked to specific oxides (Table 2). The bands Al 2p, Fe 2p, Cr 2p, Co 2p have been assigned to Al_2O_3, Fe_2O_3 (also FeOHO), Cr_2O_3 and CoO, respectively. These have already been discussed in [15]. The appearance of CoO, also noted on the similar catalyst [10], can be accounted for the thermal decomposition of Co_3O_4 which takes place in vacuum at room temperature [15,20]. Indeed, at ambient conditions, the Co_3O_4 spinel of high dispersion was recorded on the samples used in our study by Raman microscopy [15].

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 nitrate [21]. 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 Pt [21]. Although this band was a little overlapped with the other main band from Al 2p at 73.9 eV (also a doublet assigned to Al_2O_3), it clearly emerged as some sort of a shoulder on the lower energy side of the main band. For this reason, the fitting procedure described above in the experimental section was able to separate the Al 2p (3/2 and 1/2 together as overlapped doublet) broad band from the Pt 4f 7/2 and 5/2 doublet giving reliable results.

The XPS spectra were also used for quantitative analysis of the surface of the samples (Table 2). Accordingly, the majority of the exposed surface is covered with Al_2O_3. The CoO content initially increases with cobalt loading (Table 1), for the middle sample (0.3Co/CrAl) reaching a saturation value, and then decreases. Taking into account that photoelectrons come from a very superficial region, this result implies reduced dispersion of cobalt oxide on the 0.7Co/CrAl sample. The surface coverage changes upon chemisorption of Pd, which coats the surface almost totally. Judging by the changes in concentration of other oxides, PdO presumably locates more on Al_2O_3 surface rather than on CoO. 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. What is more, the Pt content on the surface of the Pt + 0.3Co/CrAl sample is on the lowest side, indicating diffusion of Pt through the Al_2O_3 matrix. The change of the chemical environment of the Pt crystallites is supportive of the relatively low value of the binding energy of Pt (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 some more inquiry.

Another view on the samples containing the unpromoted and promoted Co catalyst has been provided by contact mode AFM presented in Fig. 2. Here, we have mainly focused on determination of the surface roughness of the samples (Table 3). The shapes of some objects seen in photographs are more artefacts coming from the shape of the AFM tip scanning the surface.

One of the factors derived from AFM images to describe the morphology of surface layer is the surface roughness represented by the RMS parameter and also by relative surface area, SA (Table 3). The SA values were related to the geometric area of the images (10 μm × 10 μm). Upon depositing Co_3O_4 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 AFM results are in keeping with XPS results collected for a series of the catalysts. The parameters describing surface morphology are summarised in Table 3. There, the surface enrichment coefficient (SEC) is a ratio between content of a specific cobalt oxide calculated from XPS (Table 2) and the one calculated from LB (Table 3). These values are comparable for the 0.1 and 0.3 Co/CrAl samples and amount to about 15. The decreased value of SEC of Pd + 0.7 Co/CrAl in comparison with 0.7 Co/CrAl sample implies that Pd partly covers cobalt oxide crystallites. The decreased values of RMS and SA parameters and

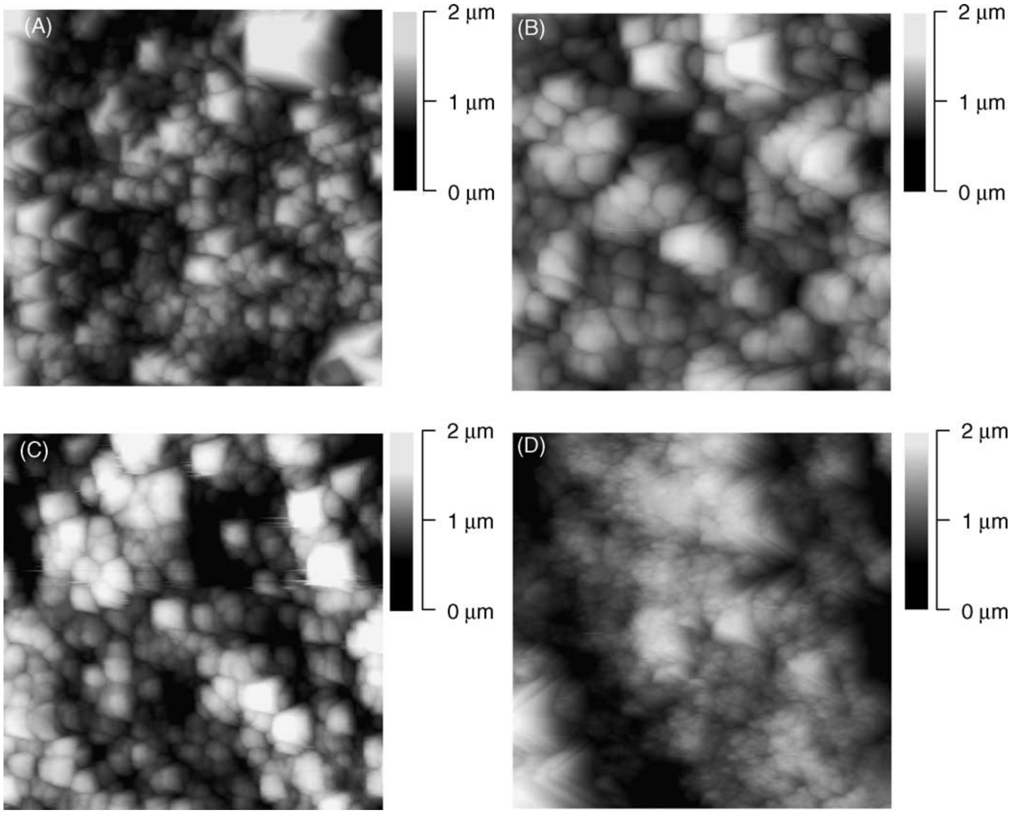

Fig. 2. AFM images of the catalysts at various stages of the preparation (10 μm × 10 μm): (A) precalcined CrAl sample; (B) 0.7 Co/CrAl sample; (C) Pt + 0.7 Co/CrAl sample; (D) Pd + 0.7 Co/CrAl sample.

increased value of SEC of Pt + 0.7 Co/CrAl, comparing to its counterparts, may suggest that Pt is situated in Al_2O_3 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 (0.1 Co/CrAl, 0.3 Co/CrAl, 0.7 Co/CrAl) and composition (promoted with Pt and Pd) are compared to those obtained for reference samples (precalcined Co foil and commercial Pt/Al_2O_3 catalyst) and presented in Fig. 3 and in Table 4. These were prepared according to the following kinetic approach. Oxidation of *n*-hexane (C6) performed in the excess of oxygen:

$$C_6H_{14} + 9\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 7H_2O \qquad (1)$$

Table 3
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	RMS (nm)	SA
CrAl	–	235	1.36
0.1 Co/CrAl	16	–	–
0.3 Co/CrAl	15	–	–
0.7 Co/CrAl	1.5	199	1.25
Pd + 0.3 Co/CrAl	15	–	–
Pd + 0.7 Co/CrAl	10	303	1.31
Pt + 0.7 Co/CrAl	4.2	155	1.21

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

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

where r is a specific reaction rate; k, the rate constant; c_{C6}, *n*-hexane concentration in the gas phase; A_{app}, a preexponential factor and E_{app}, the activation energy. The specific reaction rate, r, expressed in Eq. (2) corresponds to turn-over

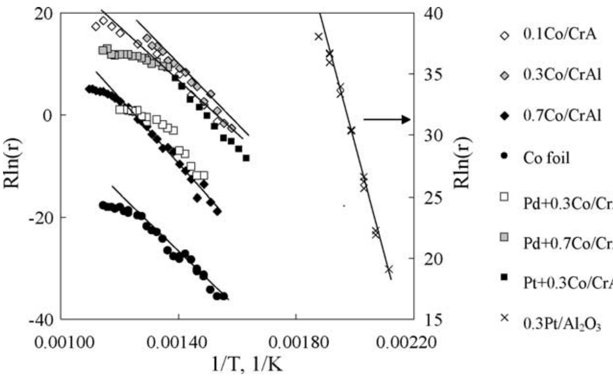

Fig. 3. Arrhenius plots prepared for the catalysts tested in *n*-hexane combustion. Description according to Table 4.

Table 4
Kinetic parameters evaluated from Arrhenius plots

Sample name	Temperature range[a] (°C)	A_{app} (1/s)	E_{app} (kJ/mol)
0.1 Co/CrAl	440–600	2.4×10^3	46
0.3 Co/CrAl	360–500	8.4×10^4	54
0.7 Co/CrAl	350–740	1.6×10^4	57
Co foil	350–570	2.2×10^2	52
Co foil (repeated experiment)	360–600	7.8×10^3	52
Pd + 0.3 Co/CrAl	460–600	35	15
Pd + 0.7 Co/CrAl	480–600	6.3×10^3	17[b]
Pt + 0.3 Co/CrAl	340–390	2.8×10^4	57
0.3 Pt/Al_2O_3	210–260	5.3×10^8	86

[a] Temperature range in which the reaction rate behaves according to Arrhenius equation.

[b] Estimated in the narrow temperature range. In the wider range 360–600 °C, E_{app} = 48 kJ/mol for this sample.

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 Co_3O_4 catalyst.

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

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

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

The superficial velocity of a gas inside the microreactor, utilised for this study, equals to 0.12 m/s and the Reynolds number derived for the hydrodynamic diameter is very low and equals to 2.4 (for an empty reactor tube diameter $Re = 7.8$). Hence, the media flow in the reactor is evidently laminar, which inevitably places the reaction in a diffusional regime, especially at higher temperatures. This is the reason why the kinetics does not reflect intrinsic catalytic reaction and is combined with diffusional effects. The calculated reaction rate and optimised kinetic parameters are thus apparent and must be treated more qualitatively than quantitatively. Additionally, the assumption of a differential reactor allowing calculating the reaction rate from C6 conversion is weaker at higher temperatures (>500 °C) when the conversion reaches 40% (a maximum conversion observed under the applied reaction conditions). Nonetheless, the apparent kinetics can be used for a rough evaluation of the catalytic performance and of the optimised reactor structures, which has been demonstrated in the accompanying paper [1].

In principle, to comprehensively describe the catalysts performance the activity should be described by a combination of three kinetic parameters: reaction rate (or preexponential factor in Arrhenius equation) at a certain temperature, activation energy and the temperature of combustion initiation.

As it has been explained above the reaction rate is not fully representative of catalyst activity due to the diffusional limitation. An illustration of the diffusional impact on the reaction rate at a low temperature are the results obtained for the reference sample of Co foil for which the catalytic tests were repeated after the sample was reloaded and repacked in the reactor (Table 4). The pre-exponential factors (A_{app}) differ over 30 times between each other. On the whole, the values of preexponential factors, which for real kinetics can be treated as a measure of the number of active centres, are extremely low and randomly distributed from one sample to another.

As regards activation energy (Fig. 3), the general trend is common for all unpromoted cobalt catalysts with an average value amounting to 52 ± 2 kJ/mol, including the results obtained for Co foil samples. By contrast, for the reference sample of the platinum supported catalyst the estimated activation energy is much higher and amounts to 86 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 (E_{app} = 17 kJ/mol in the range 460–600 °C, 48 kJ/mol in the range 330–600 °C). No such an effect was observed for the Pt-promoted sample, which did not differ in activation energy from unpromoted samples.

Eventually, the cobalt catalysts regardless their composition and loading were able to initiate the reaction at around 300 °C, which is by 100 °C higher than the platinum commercial catalyst (0.3 Pt/Al_2O_3). Similar temperature of combustion initiation was observed for propane [10], for soot [8], and for methane [13]. However, the temperature of the reaction initiation measured by us should be derived from real kinetics which would be free from diffusional limitations.

From these results it is hard to conclude, whether the reaction is structure sensitive, but a weak correlation between the catalyst loading (dispersion) and its activity can be noted. In order to exclude a possible catalytic effect coming from the precalcined CrAl carrier its activation energy and initiation temperature were estimated to be far above all studied cobalt catalysts (300 kJ/mol, initial temperature 700 °C). For the most loaded catalyst (0.7 Co/CrAl) of the lowest dispersion, the preexponential factor was the smallest, however, this effect can equally come from the diffusional limitation of the reaction rate. High activity of Pd-containing catalysts most of all should be accounted for the promoting effect of Pd which changes the reaction mechanism probably enabling oxygen adsoption on Pd centres and formation of active oxygen species. However, the increased activity can also be correlated with high surface concentration of Pd (XPS results, Table 2) and the increased dispersion of the sample (AFM results, Table 3). Conversely, no visible changes between unpromoted and Pt-promoted Co/CrAl catalysts can be explained by low surface concentration of Pt (XPS results, Table 2) and relatively low surface area and roughness coefficients (AFM results, Table 3).

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 promoting role seems a reaction initiator as it has also been suggested in [10]. Providing another type of active centres for oxygen adsorption it reduces activation energy of the overall process introducing another more efficient path into reaction network.

4. Conclusions

The Langmuir–Blodgett method used for transferring organic molecules onto the surface of precalcined chromium-aluminium steel proved suitable for depositing controlled amounts of metallic oxides of high dispersion onto the carriers surface. The cobalt catalysts prepared in this way, tested in combustion of *n*-hexane, occurred relatively active in combustion of *n*-hexane as compared to the commercial Pt/Al_2O_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 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.

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