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Supported palladium containing perovskite catalysts for methane combustion

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Citrate solution method is very suitable for preparation of multielement perovskites in the form of powders and thin layers. In this study, we demonstrate the feasibility of the method for deposition of perovskite-based materials on conventional γ-alumina and industrial metal carriers. A perovskite-based entity of $La(Co_{0.8}Ni_{0.1}Fe_{0.1})_{0.85}Pd_{0.15}O_3$ composition manifested a high catalytic activity in the methane combustion reaction. Preliminary data on the practical applicability of the perovskite-based material supported on monolithic VDM®Aluchrom Y Hf carrier are reported. Taking into account the high thermal stability of the catalytically active phase it is concluded that the prepared material can serve as a basis for further development of an effective technology for abatement of methane emissions..

Key words: palladium, cobalt perovskites, methane, complete oxidation.

INTRODUCTION

The European Union (EU) is planning reduction in the greenhouse gas emissions by 20% in 2020 as compared to 1990 [1]. Methane is a greenhouse gas (GHG) that contributes to significant share of the total amount of GHG emissions [2]. Abatement of methane emissions can be achieved by applying the method of complete catalytic oxidation. Catalysts used for methane combustion are based on palladium in combination with different metal oxides, however, the main problem related to deactivation is not solved yet.

Perovskite-type metal oxides are considered promising as catalysts for methane combustion due to their thermal stability. There has been an increasing interest in the perovskite catalysts due to the development of the so-called 'intelligent' three-way catalysts based on Pd-containing perovskite oxides [3,4], the catalytic behaviour of these catalysts being defined by palladium chemical state and redox behaviour.

Catalysts for methane combustion are usually used in the form of monoliths coated by an active phase of metal or ceramic films. The main advantages of the metal monolithic catalysts are high mechanical strength, high thermal conductivity and low thermal inertia, and low weight [5].

In this study, we present new data on synthesis and catalytic behaviour of Pd-containing Co-based perovskite oxides deposited on different industrial supports: Fe-Cr-Al – alloy wire and VDM® Aluchrom Y Hf. For comparison, conventional γ-alumina (Rhone Poulenc) was also used. The prepared catalytic systems were investigated in the reaction of complete oxidation of methane.

EXPERIMENTAL

Prior to deposition γ-alumina support was modified by SiO_2. The procedure involved impregnation of γ-alumina with silica sol (colloidal silica, 40% aqueous solution), silica content being 2 wt.% with respect to γ-alumina. Metal ions (La, Co, Ni, Fe, and Pd) from citrate solution were deposited *via* wet impregnation on silica-modified/γ-alumina support. Details on solution preparation are given elsewhere [6,7]. Pd content was 15%, while perovskite nominal composition was $La(Co_{0.8}Ni_{0.1}Fe_{0.1})_{0.85}Pd_{0.15}O_3$. The impregnated support was heated first in air at 400 °C for 3 h to decompose the citrate salts, and then the obtained solid residue was annealed in air at 600 °C for 3 h. Selected thermal treatment procedure was compatible with our own previous study on the formation of multiple-substituted perovskites having high specific surface area [6]. The weight amount of the deposited perovskite was 10%.

Industrial carriers based on Al-containing Fe-Cr alloys were used for catalyst preparation. For this purpose, Fe-Cr-Al alloy foil (or wire) was pre-oxidized at 950 °C for 10 hours to form α-alumina layer on the metal surface. The prepared catalyst carrier was coated with γ-alumina layer prepared by

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sol-gel method. On the so formed washcoat the perovskite active phase was supported by wet impregnation method.

X-ray structural analysis was performed by a Bruker Advance 8 diffractometer using CuKα radiation. Step-scan recordings for structure refinement by Rietveld's method were carried out using 2θ steps of 0.02° and 5 s duration. A FULLPROF computer program was used for calculations

TEM investigations were performed on a TEM JEOL 2100 instrument at accelerating voltage of 200 kV. Specimens were prepared by grinding and then suspending in ethanol by ultrasonic treatment for 6 min. The suspensions were dripped on standard holey carbon/Cu grids. TEM micrographs were made using digital image analysis of reciprocal space parameters. The analysis was carried out by Digital Micrograph software.

XPS measurements were carried out in the UHV chamber of ESCALAB MkII (VG Scientific) electron spectrometer applying an AlKα excitation source. Spectra calibration was performed by using the C 1s line of adventitious carbon centred at a binding energy (BE) of 285.0 eV.

Specific surface area of the catalyst samples was determined by low temperature adsorption of nitrogen according to the BET method using Nova 1200 (Quantachrome) apparatus. Temperature-programmed reduction (TPR) experiments were carried out in the measurement cell of a SETARAM DSC-111 differential scanning calorimeter directly connected to a gas chromatograph (GC), within the 300–973 K range at a 10 K/min heating rate in Ar/H_2 flow of 9:1, the total flow rate being 20 ml/min. A cooling trap between DSC and GC removed the water obtained during the reduction. To obtain *ex situ* XRD patterns of partially reduced oxides the reduction process was interrupted at selected temperatures, and then the samples were cooled down to room temperature in Ar/H_2 flow followed by argon treatment for 10 min.

The catalytic experiments were carried out at atmospheric pressure in a continuous flow type reactor equipped with mass spectrometer. The monolithic catalysts were tested as single channel reactors with inner diameter of 2.5–3.5 mm and length of 90–115 mm. For this purpose, they were placed in an isothermal tubular flow reactor. To compensate the adiabatic effect of the reaction the catalyst bed temperature was kept constant with deviations within +/–1 °C. Pressure drop of the catalyst bed was measured to be less than 1 kPa. Reactant inlet concentrations were adjusted as methane feed concentration 0.1 vol.%, oxygen 20.9 vol.%, and the feed gas mixtures were balanced to 100% with nitrogen (4.0). Gas analysis was performed using the mass spectrometer of CATLAB (Hiden Analytical) system, on-line $CO/CO_2/O_2$ gas analysers (Maihak), and THC-FID (total hydrocarbon content with a flame ionization detector, Horiba).

RESULTS AND DISCUSSION

Catalyst morphology was examined by SEM/EDS techniques. SEM images of perovskites supported on γ-alumina and monolithic VDM®Aluchrom Y Hf carrier are compared in figure 1. Deposition on γ-alumina involved formation of plate-like aggregates on the surface, however, small particles are also observable. EDS analysis indicated that the smaller particles contained mainly Pd, while the aggregates were composed of all other elements, such as La, Co, Ni, Fe, and Pd at a ratio which did not coincide with that known for nominal perovskite composition. This fact implies that during impregnation there occurs formation of a mixture of phases comprising, most probably, oxides of palladium and other metals in addition to the pure perovskite phase.

Deposition on the monolithic carrier was accomplished in the same way as in the case of γ-alumina support: there were plate-like aggregates composed of La, Co, Ni, Fe, and Pd at a ratio matching a mixture of perovskite phase and oxides of palladium, lanthanum, and transition metals. Comparison between supported catalysts shows that the deposition of the active phase on the monolithic substrate was rather inhomogeneous (Fig. 1). Needle-like network is due to the γ-alumina formed as an intermediate layer, on which the active catalytic phase of plate-like aggregates is deposited. It is important to note that irrespective of support type Pd average content in the catalysts was almost the same: 1.7 ± 0.2 wt.% on γ-alumina support and 1.2 ± 0.5 wt.% on VDM®Aluchrom Y Hf monolithic carrier.

Results from the catalytic tests are displayed in figure 2. The highest activity was observed when the perovskite phase was supported on γ-alumina in the form of irregular shaped particles (fraction 0.5–0.8 mm, Rhone Poulenc, France) followed by Fe-Cr-Al-wire (length 2.7 m, diameter 0.15 mm), the latter being used in this case as a model carrier of so called ‘wire-knitted’ catalysts.

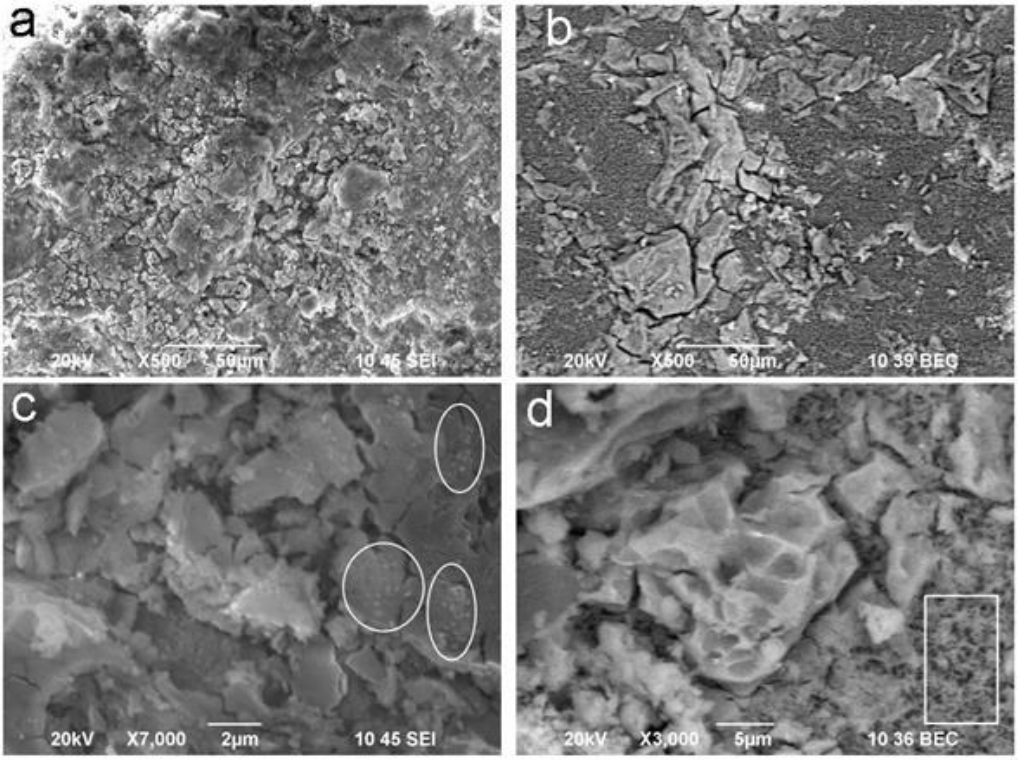

Fig. 1. SEM images of different magnification for γ-alumina (*a*,*c*) and monolithic VDM®Aluchrom Y Hf (*b*,*d*) supported catalyst. The circles indicate small particles enriched in Pd and the square points to an intermediate layer of monolithic support due to γ-alumina.

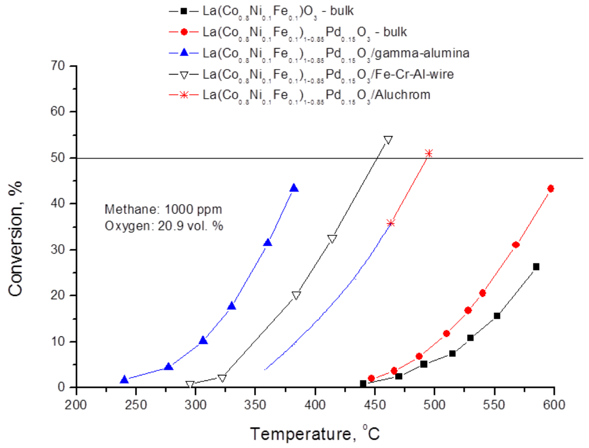

Fig. 2. Temperature dependence of conversion during complete oxidation of methane on the investigated perovskite-based catalysts.

Preliminary studies on the reaction kinetics showed that the reaction pathway over the prepared catalysts occurs most probably through Mars-van Krevelen mechanism**,** where water molecules compete with methane molecules for oxidized adsorption sites. The rate-determining step is reduction of the active sites except for the case of low oxygen concentration where reoxidation is the slower process. Despite relatively large deviation of experimental data from what is expected in the case of Eley-Rideal mechanism where the methane is impinging from the gas phase this mechanism cannot be entirely excluded since the observed reaction order to methane is close to unity.

It should be pointed out that it was assumed for both γ-alumina and Fe-Cr-Al-wire that the operation occurs under conditions of intensive mass transfer due to well-mixed gas-solid conditions (turbulent gas flow). However, for achieving methane abatement the practice requires operation with large amounts of waste gases, hence application of monolithic reactors is required. Therefore, possible application of Aluchrom is considered highly promising. Despite relatively high temperature for 50% conversion (T_{50}), about 490 °C at GHSV of 30000 h^{-1}, a combination between high thermal stability of the Pd-containing perovskite active phase and well improved thermal and corrosive resistance of Aluchrom could lead to reliable solution of the Pd-deactivation problem in parallel with low pressure drop of the catalytic element. Hence, the experimental data obtained by the Aluchrom-based monolithic catalytic tests were used for model calculations, performed by using a two-dimensional heterogeneous model for monolithic reactor, accounting for both external and internal mass transfer effects (assuming first order kinetics during isothermal operation). The principles of applied reactor modelling have been published by Belfiore [8].

Furthermore, it is of interest to calculate the needed catalyst amount for achieving a desirable degree of waste gases purification. For this purpose, the experimental results obtained by isothermal laboratory reactor were used to simulate abatement of methane containing gases under adiabatic conditions.

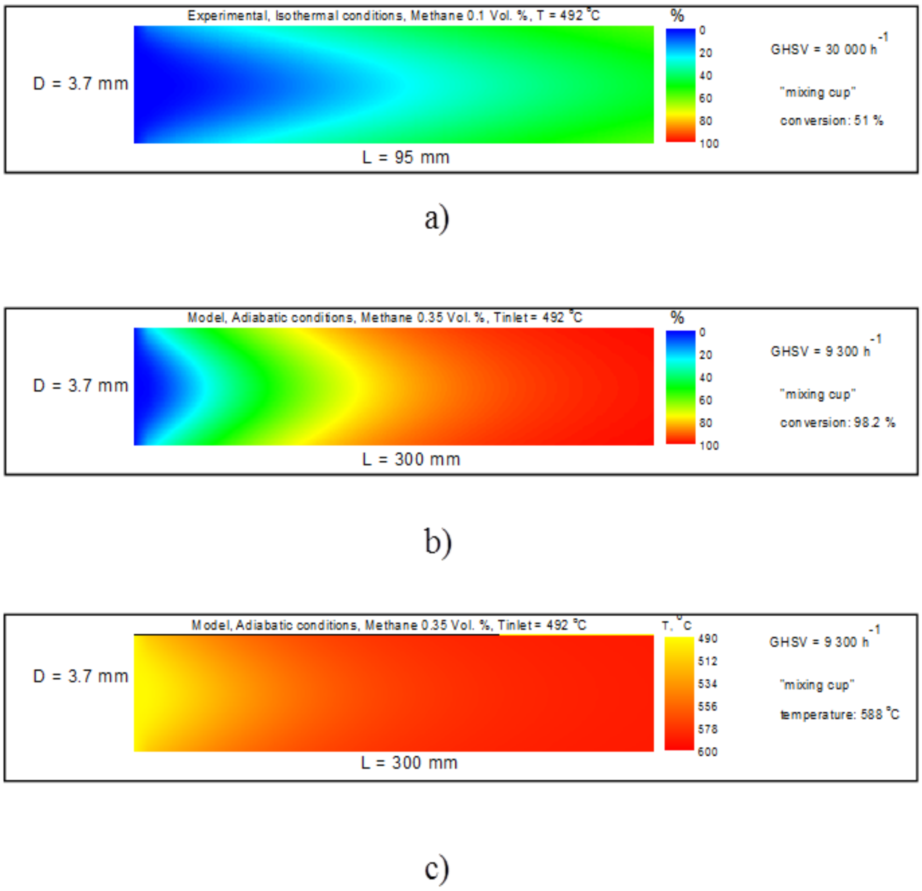

Fig. 3. Experimental data on $La(Co_{0.8}Ni_{0.1}Fe_{0.1})_{1-0.85}Pd_{0.15}O_3$/Aluchrom activity under isothermal conditions (a) and calculation of catalyst amount needed for 98.2% purification of waste gas (air) containing 0.35 vol.% methane under adiabatic conditions, (b), (c) – conversion and temperature profiles, respectively.

Due to adiabatic effect of the exothermal reaction (combustion of 0.35 vol.% methane), the temperature at reactor outlet was increased from 492 to 588 °C. Numerical investigation showed that desired conversion over 98% can be realized when the length of the monolithic element is about threefold longer than that used for laboratory experiments described above.

Experimental catalytic results and model calculations demonstrated benefits of the developed method for preparation of highly active catalysts for methane combustion.

CONCLUSIONS

Perovskite-based materials were successfully deposited on conventional γ-alumina and industrial metal carriers by impregnation using citrate solutions containing La, Co, Ni, Fe, and Pd elements. The nominal weight of deposited perovskites was 10 wt.% with respect to the support. Irrespective of support type, the average Pd content in the catalysts was almost the same: 1.7 ± 0.2 wt.% on γ-alumina support and 1.2 ± 0.5 wt.% on monolithic VDM$^{®}$Aluchrom Y Hf carrier. A uniform distribution of the active phase was achieved over the γ-alumina support.

Preliminary data on the practical applicability of $La(Co_{0.8}Ni_{0.1}Fe_{0.1})_{0.85}Pd_{0.15}O_3$ material supported on monolithic VDM$^{®}$Aluchrom Y Hf carrier were obtained. Considering the high thermal stability of the active phase it is concluded that the prepared catalyst composite is a basis for further development of an effective technology for abatement of methane emissions.

Established correlations concerned with synthesis history, structure, and morphology of the catalysts and their catalytic activities are of significance in order to design more effective monolith catalysts for the reaction of methane combustion at relatively low temperatures.

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НАНЕСЕНИ ПАЛАДИЙ СЪДЪРЖАЩИ ПЕРОВСКИТОВИ КАТАЛИЗАТОРИ ЗА ПЪЛНО ОКИСЛЕНИЕ НА МЕТАН

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(Резюме)

Методът на основата на цитратни разтвори е подходящ за получаване на многоелементни перовскити под формата на прахове и тънки слоеве. В това изследване показваме приложимостта на този метод за отлагане на перовскит-съдържащи материали върху конвенционални γ-алуминиеви и промишлени метални носители. Перовскитовият катализатор с номинален състав на активния компонент $La(Co_{0.8}Ni_{0.1}Fe_{0.1})_{0.85}Pd_{0.15}O_3$ показва висока каталитична активност в реакцията на изгаряне на метан. Представени са предварителни данни за практическата приложимост на катализатор с монолитен носител VDM®Aluchrom Y Hf. Благодарение на високата си термична стабилност, предложената активна фаза може да служи като основа за разработване на ефективна технология за намаляване на емисиите на метан.