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Spectroscopic characterization of Co_3O_4 catalyst doped with CeO_2 and PdO for methane catalytic combustion ☆

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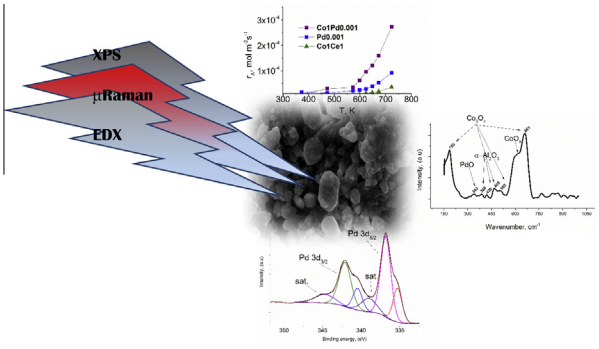
HIGHLIGHTS

- μRaman, XPS and EDX methods used to analyze catalyst material distribution.
- Palladium doped cobalt catalyst shows amazingly high activity in methane combustion.
- Surface of palladium doped catalyst covered with highly dispersed PdO.

GRAPHICAL ABSTRACT



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ABSTRACT

The study deals with the XPS, Raman and EDX characterization of a series of structured catalysts composed of cobalt oxides promoted by palladium and cerium oxides. The aim of the work was to relate the information gathered from spectroscopic analyses with the ones from kinetic tests of methane combustion to establish the basic structure–activity relationships for the catalysts studied. The most active catalyst was the cobalt oxide doped with little amount of palladium and wins a confrontation with pure palladium oxide catalyst which is commercially used in converters for methane. The analyses Raman and XPS analyses showed that this catalyst is composed of a cobalt spinel and palladium oxide. The quantitative approach to the composition of the catalysts by XPS and EDX methods revealed that the surface of palladium doped cobalt catalyst is enriched with palladium oxide which provides a great number of active centres for methane combustion indicated by kinetic parameters.

Introduction

From a wide spectrum of methods which are used in waste gases cleaning, catalytic combustion seems to be the most effective approach especially in the case of low concentration of methane and carbon monoxide. These pollutants appear in several

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stationary sources utilizing biogas that can be obtained from biomass or methane as for example from a shale gas or coal mines. It seems that the conditions of the catalytic combustion are less demanding than those of classic homogeneous combustion: undoubtedly catalytic process runs at lower temperature and more flexible air/fuel ratio [1].

For methane combustion, catalysts based on palladium oxide are the most likely used and a lot of attention has been given to such systems in the literature, as described in [2]. Besides palladium, which is claimed to be the most active in this reaction, a great deal of research has been performed to test different metal oxides. In the literature high catalytic activity of Co_3O_4, AgO, CuO, MnO, Cu/CeO_2, Ag/CeO_2, MnO_X/ZrO_2 was reported as for example in Ref. [3]. Moreover, great activity of mixed metal oxide systems was also reported elsewhere [4]. For example, the catalytic activity of the composite catalysts were studied during the combustion of CH_4 (3000 ppm) in a mixture of oxygen and helium. High activity in methane combustion was also fulfilled by using a mixed

Table 1
Catalysts preparation parameters.

Catalyst	Number of active agents	Solution used for immersion	Impregnation time (h)
Co1	1	1 M $Co(NO_3)_2$	1
Co1Pd0.001	2	1 M $Co(NO_3)_2$ 0.001 M $Pd(NO_3)_2$	1
Co1Ce1	2	1 M Co(NO3)2 1 M Ce(NO3)3	1
Pd0.001	1	0.001 M $Pd(NO_3)_2$	1

Table 2
Semi-quantitative results of XPS and EDX analysis.

Method	Catalyst	Wt.%				At.%			
		Al*	Ce	Co	Pd	Al*	Ce	Co	Pd
XPS	Co1	69.4	–	30.6	–	83.2	–	16.8	–
	Co1Pd0.001	75.4	–	0.0	24.6	92.4	–	0.00	7.63
	Co1Ce1	30.0	0.0	70.0	–	48.3	0.0	51.7	0.00
	Pd0.001	11.5	–	–	88.5	33.8	0.0	0.00	66.17
EDX	Co1	49.6 ± 0.3	–	50.4 ± 0.5	–	68.21 ± 0.02	–	31.79 ± 0.01	–
	Co1Pd0.001	66.2 ± 0.3	–	31.1 ± 0.5	2.7 ± 0.3	81.60 ± 0.03	–	17.54 ± 0.02	0.85 ± 0.08
	Co1Ce1	9.9 ± 0.3	18.70 ± 0.50	71.4 ± 1.2	–	21.42 ± 0.06	7.80 ± 0.02	70.78 ± 0.03	–
	Pd0.001	96.6 ± 0.3	–	–	3.4 ± 0.3	99.12 ± 0.39	–	–	0.88 ± 0.10

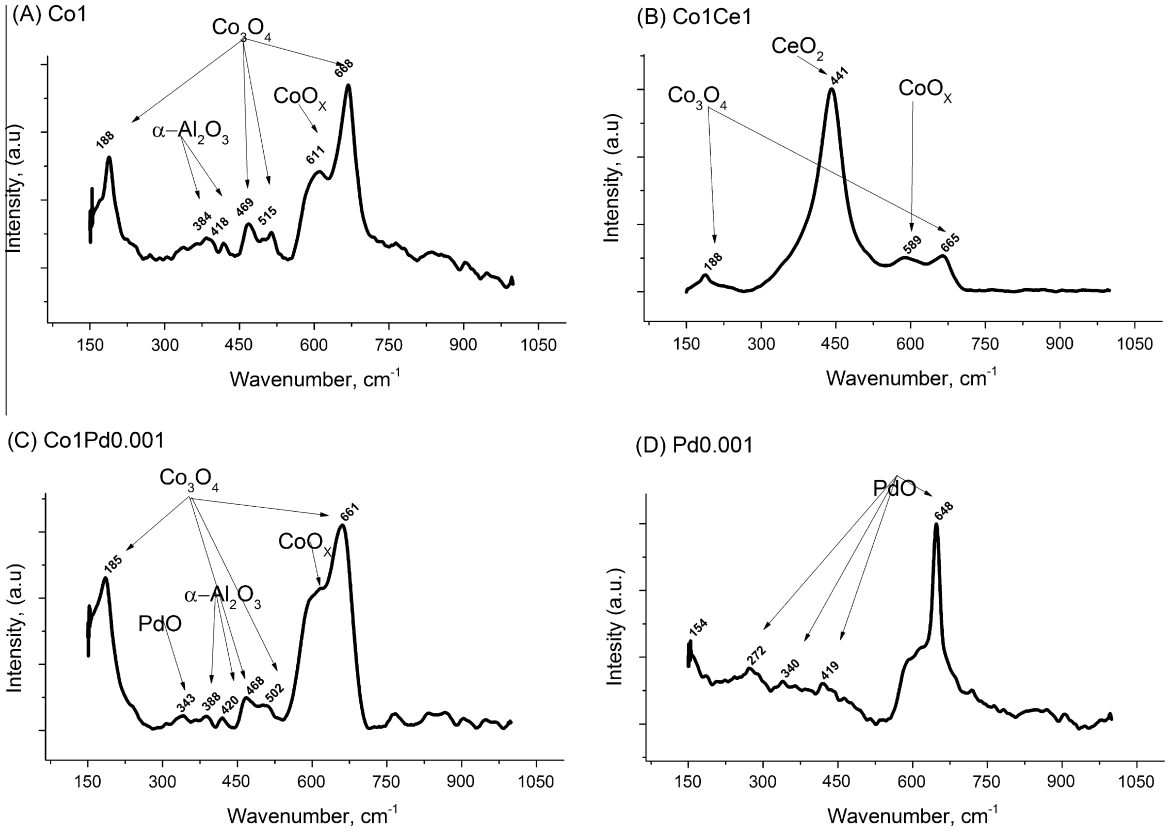

Fig. 1. Raman spectra of prepared samples.

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