

**Studies of Zn-Al-Ce mixed oxides as catalysts
for diesel soot combustion ***

L. Chmielarz¹, A. Węgrzyn¹, A. Kowalczyk¹, S. Witkowski¹,
R. I. Walton² and A. Matusiewicz³

¹*Faculty of Chemistry, Department of Chemical Technology,
Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland
tel. +48-12 663-20-06; fax: +48-12 634-05-15;
e-mail: chmielar@chemia.uj.edu.pl*

²*Department of Chemistry, The University of Warwick, Coventry, CV4 7AL, UK*

³*The Institute of Ceramics and Building Materials, Glass and Building
Materials Division, Cementowa 8, 31-983 Kraków, Poland*

A series of Zn-Al-Ce mixed oxides was synthesized by a co-precipitation method. The obtained samples were characterized with respect to composition (XRF), structure (XRD, FT-IR) and texture (BET). Zn-Al-Ce mixed oxides were tested as catalysts of diesel soot combustion. The best catalytic activity was found for Zn₂Ce oxide system, which operated in the temperature range of 350–500°C.

1. INTRODUCTION

Currently, diesel vehicles are widely used due to high fuel efficiency. However, soot particulates, nitrogen oxides (NO_x = NO + NO₂), carbon monoxide and unburned hydrocarbons are the main pollutants produced in the combustion of diesel fuels. Carbon monoxide as well as unburned hydrocarbons may be easily catalytically oxidised to CO₂ and H₂O. Abatement of soot produced in diesel engines commonly consists of the mechanical filtration of carbonaceous particles using diesel particulate filter (DPF) and their subsequent combustion to avoid pressure drops caused by plugging of the filter. The

*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

temperature required for the soot combustion is 500-600°C, whereas the temperature of exhaust gases in a typical diesel engine is in the range of 150–450°C. Therefore, there is a need to develop effective catalyst which will be able to decrease the temperature of carbonaceous particles burning.

Various types of catalytic materials, including metal oxides [e.g. 1, 2], precious metals [e.g. 3, 4] and modified mineral materials [e.g. 5] were tested in the process of soot combustion. In a group of metal oxides, ceria based systems were recognised as active catalysts of the carbonaceous particles combustion due to high availability of surface oxygen and high surface reducibility [6-8]. Ceria has the ability to change oxidation state in the cycle $\text{CeO}_2 \leftrightarrow \text{CeO}_{2-x}$ during operation, allowing the oxygen uptake and the release to occur. Therefore, CeO_2 is one of the most promising components of catalysts for combustion of soot particles.

2. MATERIALS AND METHODS

Materials. Printex-U (Evonik Degussa GmbH, Germany) was used as model carbonaceous soot particles. The BET surface area of soot particles was 96 m²/g with an average particle diameter of 20 nm. It contained approximately 8.1 wt.% of volatile matter, 0.9 wt.% of wetness and about 0.1 wt.% of ash.

A series of Zn-Al-Ce mixed oxides was obtained by a co-precipitation method. Aqueous solutions containing various molar ratios of Zn/Al/Ce cations were prepared using corresponding metal nitrates. A solution of NaOH (10%) was used as a precipitating agent. The pH of the obtained mixtures was kept in the range of 7.8-8.2. In the next step precipitates were aged at 70°C for 2 hours and then separated by filtration, washed with distilled water, oven dried and finally calcined at 450°C for 12 hours.

Nanocrystalline CeO_2 was used as a reference catalyst. A suitable amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water to obtain a solution of 0.04 M. The pH of the obtained solution was adjusted to 1.9 by addition of HCl (37%). Then H_2O_2 was added into the solution to obtain the molar Ce: H_2O_2 ratio of 1:10. After 30 minutes of stirring, a solution of NaOH (1 M) was added stepwise. The obtained slurry was aged at room temperature for 2 hours. Then precipitate was separated by filtration, washed with distilled water, dried at room temperature and finally calcined at 500°C for 3 hours.

Catalysts characterization. Chemical compositions of the catalyst samples were determined by XRF using an Axios Cement instrument (Panalytical). Prior to the analysis the samples were calcined at 900°C.

BET surface areas of the calcined samples were determined using a Quantasorb Jr. (Ankersmith).

The X-ray diffraction patterns of the catalysts' precursors and catalysts were acquired with a Siemens D5000 diffractometer operating with Cu K α radiation (average wavelength = 1.54056 Å).

FTIR spectra of the catalysts' precursors were recorded with a Bruker IFS 48 spectrometer using the KBr pellet technique.

Catalytic tests. The catalytic activity for the carbonaceous soot combustion was studied by temperature programmed oxidation (TPO) of catalysts-soots mixtures. Each catalyst was ground thoroughly with soots (weight ratio of catalyst:soots – 9:1) in a mortar for 5 minutes in order to achieve a tight contact between the mixture components. The blank experiment was studied for the reference sample obtained by mixing of quartz powder with soots (ratio – 9:1) in a mortar. The tight contact conditions are poorly represented in real working conditions but they allow a fast screening of the catalytic performance of the tested samples under reproducible experimental conditions.

In each run 20 mg of catalyst-soot sample was heated at a constant rate (10°C/min) from 100 to 700°C in a quartz reactor. A flow of gas mixture containing 3.6% of O₂ diluted in helium was supplied to the reactor at a total flow rate equal 40 ml/min. The process of carbon soot oxidation was monitored by QMS (VG-QUARTZ) connected directly to the reactor outlet. The mass-to-charge (m/z) ratios characteristic for CO₂ (m/z=44), CO (m/z=28), O₂ (m/z=32, 16), H₂O (m/z=18) and He (m/z=4) were continuously monitored. The reactor temperature was controlled by temperature programmer (Eurotherm 3216) via K-type thermocouple (Omega) located on the catalyst bed.

3. RESULTS AND DISCUSSION

Chemical composition of the calcined samples as well as their BET surface area is presented in Table 1. It should be noted that measured surface area for the mixed oxide is in the range of 30–63 m²/g, while for the reference nano-CeO₂ sample is only 19 m²/g.

The phase composition of the catalysts' precursors was studied using XRD method. The examples of X-ray diffractograms are presented in Figure 1, while assignments of reflections representative for the identified phases are shown in Table 2. For all the Ce- and Zn-containing samples reflexes characteristic for the presence of the CeO₂ and ZnO phases were detected. In the case of Zn₂Al sharp and intensive reflections related to the hydrotalcite-like phase were identified. Such reflections, however significantly less intensive, were also present in diffractograms of the other samples containing both aluminium and zinc. Therefore, it could be concluded that CeO₂ and ZnO exist as separate oxides, while aluminium and a fraction of zinc form the hydrotalcite-like phase. For

comparison, diffractogram recorded for nano-CeO₂ is presented in Figure 1. The broadening of the reflections at 2θ about 28.6° and 47.8° compared with the relatively low specific surface area suggest that the mean CeO crystallite is built by aggregation of very fine monocrystals. During further treatments CeO₂ may partly sinter giving diffraction peaks of significantly lower width in calcined catalysts.

Tab. 1. Chemical composition and specific surface area of the Zn-Al-Ce catalysts.

Sample code	Mixed metal oxide	Metal oxides content [wt.%]			BET surface area [m ² /g]
		ZnO	Al ₂ O ₃	CeO ₂	
Zn ₂ Al	(ZnO) ₂ (Al ₂ O ₃) _{0.5}	76.2	23.8	–	45
Zn ₂ Al _{0.75} Ce _{0.25}	(ZnO) ₂ (Al ₂ O ₃) _{0.375} (CeO ₂) _{0.25}	66.7	15.7	17.6	30
Zn ₂ Al _{0.5} Ce _{0.5}	(ZnO) ₂ (Al ₂ O ₃) _{0.25} (CeO ₂) _{0.5}	59.3	9.3	31.4	63
Zn ₂ Al _{0.25} Ce _{0.75}	(ZnO) ₂ (Al ₂ O ₃) _{0.125} (CeO ₂) _{0.75}	53.4	4.2	42.4	44
Zn ₂ Ce	(ZnO) ₂ CeO ₂	48.6	–	51.4	40
nano-CeO ₂	CeO ₂	–	–	100.0	19

The examples of the FT-IR spectra recorded for the catalysts' precursors (samples before calcination) are presented in Figure 2. For all the samples bands characteristic for hydroxyl groups and adsorbed water at 3300-3500, 1630 and below 700 cm⁻¹ were detected. For the samples containing the hydrotalcite phase the high intensity of the band located at 3440 cm⁻¹ and related to the presence of OH groups was identified. The increase of Ce substitution resulted in the shift of described band to 3280 cm⁻¹. Therefore, it is possible that the latter band should be assigned to H-bonded water molecules. The band of bending modes of water molecules was found at around 1630 cm⁻¹.

The most informative range of the recorded spectra is between 1800–500 cm⁻¹. For the hydrotalcite-containing precursors, bands characteristic for interlayer anions were observed at 1384–1379 and 1354 cm⁻¹, which correspond to stretching vibrations of NO₃⁻ and CO₃²⁻ anions, respectively. Additional bands assigned to nitrates were observed at 1765 and 825–834 cm⁻¹, and for carbonates – at 867 cm⁻¹ [9]. In the materials with higher content of CeO₂ crystalline phase another overlapping bands were observed at 1340 and 1495 cm⁻¹. Those bands may be related to the presence of carbonates. It has been reported [10, 11] that CO₂ adsorb on the ceria surface and “carbonate-like” species are formed. The same origin has been suggested for the band placed at 1058 and 840 cm⁻¹.

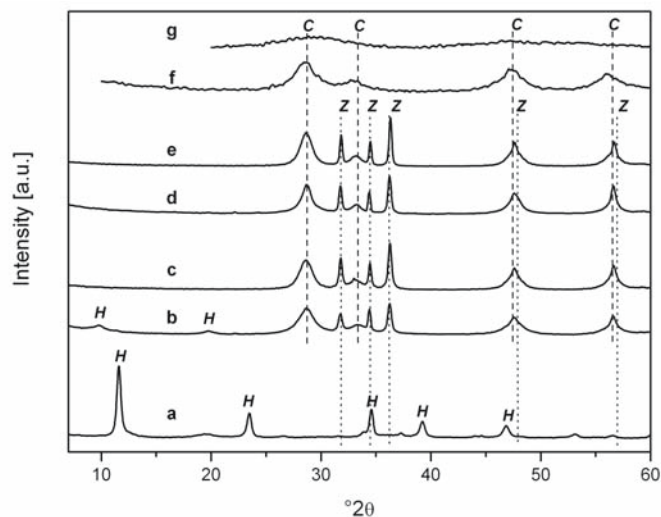


Fig. 1. Structure of catalysts' precursors: a – Zn_2Al , b – $\text{Zn}_2\text{Al}_{0.25}\text{Ce}_{0.75}$, d – Zn_2Ce , f – CeO_2 , g – nanocrystalline CeO_2 , and catalysts (calcined samples): c – $\text{Zn}_2\text{Al}_{0.25}\text{Ce}_{0.75}$, e – Zn_2Ce ; phase identification: C – CeO_2 , Z – ZnO , H – hydrotalcite.

Tab. 2. Positions of the reflections recorded in the phase identification (CeO_2 , ZnO , hydrotalcite).

CeO_2	$^{\circ}2\theta$	ZnO	$^{\circ}2\theta$	HT	$^{\circ}2\theta$
	28.6		31.8		9.2 – 11.6
	33.3		34.4		19.7 – 23.2
	47.8		36.8		34.5
	56.4		47.6		39.2
			56.6		46.8
			62.9		60.3
					61.7

It should be noted that the intensity of the band related to “carbonate-like” species increases with an increase of cerium content. The FT-IR studies confirm that CeO_2 exist as a separate phase, what is consistent with the results of XRD analysis.

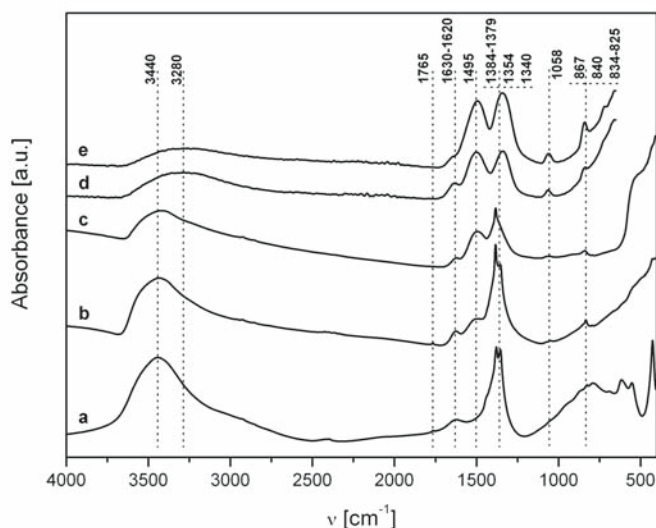


Fig. 2. Infrared spectra of catalysts' precursors: a – Zn_2Al , b – $\text{Zn}_2\text{Al}_{0.25}\text{Ce}_{0.75}$, c – Zn_2Ce , d – nanocrystalline CeO_2 , e – CeO_2 .

Catalytic soot combustion was studied under TPO conditions in a flow microreactor system. The results of these studies are presented in Figure 3. Carbon dioxide and water vapour were the only detected reaction products. The oxidation of carbon soot particles without catalyst (mixture of quartz powder and soot particles) started at 510°C, while for the complete combustion temperature of 780°C was necessary. The process of carbonaceous soot oxidation was catalysed by mixed Zn-Al-Ce oxides. An increase in the Ce-content significantly activated those oxide systems in the process of soot particles combustion. The best results were found for the Zn_2Ce catalyst, which effectively operated at temperature below 490°C. Since, in a series of the tested samples the highest activity was found for the catalysts with high cerium content therefore, nanocrystalline CeO_2 was used as a reference sample. It should be noted that this sample presented significantly lower activity than the Zn_2Ce catalyst.

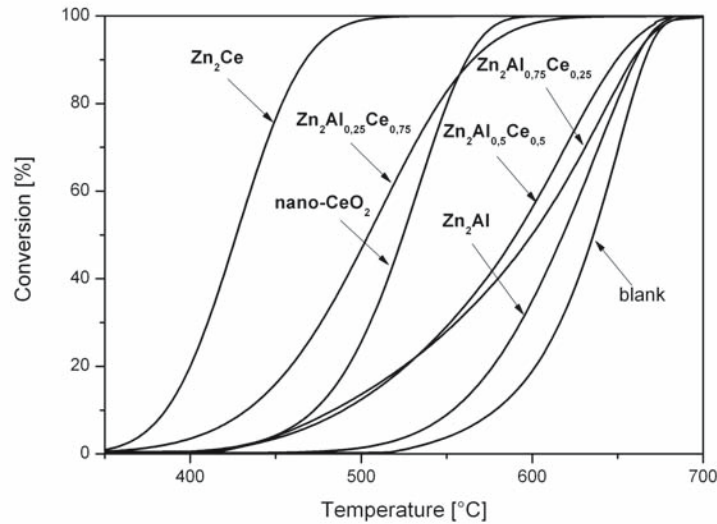
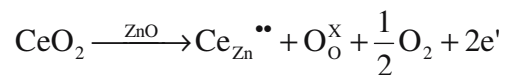


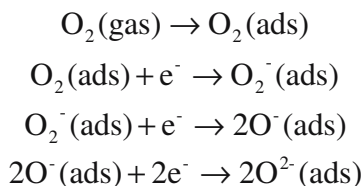
Fig. 3. Results of the carbonaceous particles combustion over Zn-Al-Ce catalysts.

As it was shown by XRD studies, for the most catalytically active sample – Zn_2Ce , two coexisting phases – ZnO and CeO_2 – were found. On the other hand, the nanocrystallite CeO_2 sample presented significantly lower catalytic activity than the Zn_2Ce catalyst. Therefore, it seems that the high activity of the Zn_2Ce catalyst is related to the presence of ZnO phase. However, it should be also noted that cerium, in contradiction to aluminium, increased the activity of the catalysts. Ge et al. [12] have shown that it is possible for Ce^{4+} to replace Zn^{2+} partially in the ZnO structure due to similar ionic radius ($\text{Zn}^{2+}=0.74 \text{ \AA}$, $\text{Ce}^{4+}=0.96 \text{ \AA}$). Substitution takes place according to the following defect reaction:



where $\text{Ce}_{\text{Zn}}^{\bullet\bullet}$ is the substituent cerium ion Ce^{4+} in the Zn^{2+} position in the ZnO lattice and O_0^{\times} stands for the oxygen O^{2-} ion in the anionic position. For each cationic site, ZnO structure offers just one anionic and therefore the second oxygen originally bound to Ce^{4+} cannot be incorporated. In order to fulfil electro neutrality rule in this reaction, two electrons from the second oxygen ion are kept in ZnO structure. These extra electrons are supplied into the conductive band what decreases ZnO resistance [e.g. 12]. Low-temperature combustion of carbonaceous particles needs reactive oxygen species formed on the catalysts'

surface. Various possible forms of surface oxygen species including O_2^- , O^- and O^{2-} have been reported in scientific literature [e.g. 13]. The chemisorption and activation of oxygen molecules on the catalyst surface can be presented in the form of the following reactions:



These reactions create oxygen adsorbates and deplete electrons from the conduction band of ZnO. The studies of Ge et al. [12] have shown significant increase in the resistance of ZnO partially substituted with Ce^{4+} cations after oxygen chemisorption. The resistance of this sample was significantly higher than that measured for pure ZnO and depended on the chemisorption temperature. Therefore, it could be concluded that ZnO partially substituted with Ce^{4+} cations effectively activate oxygen for the reaction with carbonaceous particles.

Another explanation of high activity of the Zn_2Ce catalyst could be related to improvement of the redox properties of CeO_2 partially substituted with Zn^{2+} cations. Such effect has been reported by Balducci et al. [14] for various divalent cations, including Zn^{2+} . It has been shown that the modification of the redox properties depends on the radius of divalent cations. Substitution of smaller cations for Ce^{4+} into CeO_2 improved the redox properties more effectively. This effect was less significant for larger divalent cations and also for trivalent cations.

4. SUMMARY

In presented studies it was shown that mixed Zn-Al-Ce oxide system was effective in the soot combustion process. Substitution of cerium by aluminium resulted in an increase of specific surface area of the catalysts. However, catalytic activity was correlated with the cerium content. The Zn_2Ce sample was found to be the most active catalyst. For this sample two coexisting phases – ZnO and CeO_2 – were identified. It was suggested that partial replacement of zinc cations by cerium in ZnO structure is responsible for more effective activation of chemisorbed oxygen molecules for soot combustion. Another possible explanation for higher activity of Zn-Ce oxide system with respect to

pure ceria may be modification of its redox properties due to CeO₂ doping with Zn²⁺.

5. REFERENCES

- [1] D. Fino, N. Russo, G. Saracco, V. Specchia, *J. Catal.*, 242, 38 (2006).
- [2] S. Li, R. Kato, Q. Wang, T. Yamanaka, T. Takeguchi, W. Ueda, *Appl. Catal. B* 93, 383 (2010).
- [3] J. Uchisawa, A. Obuchi, A. Ochi, T. Nanbara, N. Nakayama, *Powder Technol.* 180, 39 (2008).
- [4] B. S. Sánchez, C. A. Querini, E. E. Miró, *Appl. Catal. A*, 366, 166 (2009).
- [5] N. Güngör, S. Işçi, E. Günister, W. Miśta, H. Tetrycz, R. Klimkiewicz, *Appl. Clay Sci.* 32, 291 (2006).
- [6] M. L. Pisarello, V. Milt, M. A. Peralta, C. A. Querini, E. E. Miró, *Catal. Today* 754, 65 (2002).
- [7] V. G. Milt, C. A. Querini, E. E. Miró, M. A. Ulla, *J. Catal.*, 220, 424 (2003).
- [8] J. Setiabudi, G. Chen, M. Mul, J. A. Makkee, J. A. Moulijn, *Appl. Catal. B*, 51, 9 (2004).
- [9] A. Węgrzyn, A. Rafalska-Łasocha, D. Majda, R. Dziembaj, H. Papp, *J. Therm. Anal. Calorim.* 99, 443 (2010).
- [10] K. M. S. Khalil, L. A. Elkabee, B. Murphy, *Micropor. Mesopor. Mater.* 78, 83 (2005).
- [11] M. Zawadzki, *J. Alloys Compd.*, 454, 347 (2008).
- [12] C. Ge, C. Xie, S. Cai, *Mater. Sci. Eng.* 157, 53 (2007).
- [13] M. F. Al-Kuhaili, A. M. A. Durrani, I. A. Bakhtiari, *Appl. Surf. Sci.* 255, 3033 (2008).
- [14] G. Balducci, M. S. Islam, J. Kašpar, P. Fornasiero, M. Graziani, *Chem. Mater.* 15, 3781 (2003).

CURRICULA VITAE



Lucjan Chmielarz. Born in Poland in 1966. Graduated from the Jagiellonian University in Krakow (1992). Received his Ph.D. and D.Sc. degree (1997 and 2007, respectively) in chemistry from the Jagiellonian University. He is a head of Environmental Protection studies at JU (since 2008) and head of Group of Chemical Environmental Technologies (since 2008). Member of Polish Chemical Society (since 2005), Polish Catalysis Club (since 2005) and Polish Zeolite Association (since 1999). He specializes in synthesis and characteristics of micro- and mesoporous materials with controlled porous structure for catalysis and adsorption as well as catalytic processes for purification of flue gases.



Agnieszka Węgrzyn, born in Krakow in 1975. Graduate of Jagiellonian University. She received her Ph.D. degree in chemistry from the Jagiellonian University in Krakow in 2005. Research fellow at University of Leipzig (2004/2005), University of Warwick (2007), assistant professor in Ecole Nationale Supérieure des Mines de Saint-Étienne (2010). Specialization: environmental chemistry, synthesis of advanced materials for catalysis and adsorption, removal of contaminants from water.



Stefan Witkowski. Born in 1960. Graduated from the Jagiellonian University in Krakow 1984. Ph.D. 1998 in chemistry from the Jagiellonian University in Krakow. Specialization: nanomaterials, physico-chemical characterization, heterogeneous catalysis.