The use of $\text{CeO}_2\text{-Co}_3\text{O}_4$ oxides as a catalyst for the reduction of N_2O emission

Maria Rajska^{1,a}, Bartosz Wójtowicz¹, Łukasz Klita¹, Łukasz Zych¹ and Rafał Zybała²

¹AGH University of Science and Technology, Faculty of Materials Science and Ceramic, Al. Mickiewicza 30, 30-059 Krakow, Poland

²Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland

Abstract. The morphological characterization of a series of cobalt-cerium oxide composites prepared by the deposition of CeO_2 onto Co_3O_4 powder with a molar ratio of cerium oxide to Co_3O_4 in the range of 0 to 1 was performed. The powders were also impregnated with a solution of K_2CO_3 to obtain the theoretical content of potassium atoms $2\text{at}\cdot\text{nm}^{-2}$. To investigate the effect of adding specific amount of CeO_2 on the catalytic activity, the X-ray diffraction, SEM-EDX, laser particle size distribution and BET surface area measurements were used. The catalysts were tested through the low-temperature decomposition of nitrous oxide in the temperature range of 50°C to 700°C . The addition of CeO_2 and K always moved the temperature of a complete N_2O conversion towards lower temperatures (480°C - 540°C to 340°C - 420°C). The best catalytic properties were shown by the samples in which the ratio of cerium oxide to cobalt oxide ranged from 0.4 to 0.7.

1 Introduction

N_2O emission to the atmosphere is considerably less intense than in the case of other greenhouse gases, but the GWP (Global Warming Potential) of nitrous oxide is 310 times higher than for carbon dioxide [1]. It is estimated that the current contribution of N_2O oxide to the total greenhouse effect is approximately 6.5 vol.% [2]. Nitrous oxide has the ability to accumulate infrared radiation and indirectly destroy the ozone layer through the chemical reactions of substances formed from N_2O . In the upper stratosphere, compounds derived from nitrous oxide, reacting readily with ozone, are formed, thus destroying the natural protective layer of the Earth [3].

The reduction of N_2O can be carried out in two different temperature ranges, which resulted in selecting catalysts suitable for the pre-defined reaction conditions. In terms of higher temperatures, i.e. these ranging from 800°C to 900°C , for the reduction of N_2O systems characterized by good thermal stability, including spinels, perovskites and mayenite [4-9], are used. For the lower temperature range between 250°C and 450°C , zeolites, known as oxide catalysts with a high specific surface area and a small amount of precious metals or transition metal oxides are applied [10-13]. It was found that cordierite could be a very good catalyst support for other catalytically active phases in deN_2O reaction [14]. This kind of catalysts, based on spinel $\text{K/Zn-Co}_3\text{O}_4$ are successfully checked in pilot plant conditions, with maintaining thermal stability, structure, morphology and high catalytic activity [15].

Lowering of the temperature of the N_2O reduction reaction is economically advantageous, at the same time meaning other chemical composition of the catalyst than in the case of high-temperature reduction. At present, catalysts with different promoters used for the low-temperature reduction of N_2O have to act selectively in a catalytic reduction process [1]. The catalysts based on a Co-Ce oxide composite with different promoters were prepared. The alkali metals (Na, K, Rb, Cs) showed a better catalytic activity in the case of the low-temperature reduction of N_2O than the alkaline earth metals (Mg, Ca, Sr, Ba). The promotion effect followed the $\text{Li}<\text{Na}<\text{K}<\text{Rb}<\text{Cs}$ order for the alkali metals, and the $\text{Mg}<\text{Ce}<\text{Sr}<\text{Ba}$ order for the alkaline earth metals. The alkali metals may act as electronic promoters and thus could be improved the redox ability Co^{2+} [1]. Grzybek and co-workers analysed a series of $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts prepared by the incipient wetness impregnation of CeO_2 . The Co-Ce catalyst (1 wt.% Co_3O_4 -1 wt.% CeO_2) exhibits the highest apparent reaction rate per mass of Co_3O_4 . The authors proposed an explanation that the observed phenomenon entailing the high catalytic activity of the $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalyst with 1 wt.% content results from the dispersion effect. The catalytic activity of the Co-Ce composites was intensified as a consequence of facilitating the electron donation process, which improved the reducibility of Co^{3+} to Co^{2+} [16]. It was found that the catalysts with a high efficiency during the low-temperature N_2O reduction reaction contained rhodium supported on zirconia, praseodymium-doped ceria or mixed systems incorporating titanium oxide and cerium oxide, additionally coated with rhodium

^a Corresponding author: rajska@agh.edu.pl

[17-19]. However, research into the cobalt-based catalysts and promoted alkali metals: sodium and potassium shows that it is possible to achieve complete conversion at a temperature below 450°C [20,21]. Such catalysts are very active in this reaction and do not contain precious metals, which consequently further reduces their cost [22]. The presence of potassium ions significantly improves the catalytic properties of cobalt-containing catalyst systems or manganese spinels [23,24]. Potassium-promoted cobalt spinel catalysts obtained from the K_2CO_3 precursor have both high stability and low work function [23].

In the present work, we report on the catalytic activity of a series of K-promoted Co-Ce oxide composites with the molar ratio of CeO_2/Co_3O_4 oxides ranging from 0 to 1 respectively. We try to find the optimum range of molar participation of two oxides forming a composite material.

2 Experimental

A series of Co-Ce composite oxide catalysts was prepared by the deposition of CeO_2 onto Co_3O_4 powder (99%, Merc), as shown in Table 1. Samples were obtained through the precipitation of the precursor of CeO_2 ($Ce(NO_3)_3 \cdot 6H_2O$) on the Co_3O_4 powder at $pH = 10 \pm 1$ using a 3M ammonia solution [25,26]. The resultant precipitate was aged for two hours at room temperature and then several times eluted from the excess of hydroxide ions to obtain the near-neutral pH. The slurry prepared in this manner was dried for 12 hours at 40°C and calcined for 3 hours at 500°C [27]. The resultant powders have a different molar content of CeO_2 (from 0.0 to 1.0 mol) and a constant content of Co_3O_4 (1 mol).

The impregnation of the catalysts was made using the dry impregnation method with $2K_2CO_3 \cdot 3H_2O$ (to obtain 2 atoms $K \cdot nm^{-2}$) in an amount sufficient to fill the pores of the support [28]. Before performing the impregnation of each sample the sorption capacity was measured twice by titrating the carrier in distilled water.

Table 1. The sample symbols.

Sample	Before impregnation	After impregnation
Co_3O_4	Co	Co_K
$Co_3O_4-0.1CeO_2$	Co0.1Ce	Co0.1Ce_K
$Co_3O_4-0.2CeO_2$	Co0.2Ce	Co0.2Ce_K
$Co_3O_4-0.3CeO_2$	Co0.3Ce	Co0.3Ce_K
$Co_3O_4-0.4CeO_2$	Co0.4Ce	Co0.4Ce_K
$Co_3O_4-0.5CeO_2$	Co0.5Ce	Co0.5Ce_K
$Co_3O_4-0.6CeO_2$	Co0.6Ce	Co0.6Ce_K
$Co_3O_4-0.7CeO_2$	Co0.7Ce	Co0.7Ce_K
$Co_3O_4-0.8CeO_2$	Co0.8Ce	Co0.8Ce_K
$Co_3O_4-0.9CeO_2$	Co0.9Ce	Co0.9Ce_K
$Co_3O_4-1.0CeO_2$	Co1.0Ce	Co1.0Ce_K

2.1 Methods

The morphology of the particles was investigated using

scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX) using the NOVA NANO SEM 200 scanning electron microscope from FEJ EUROPE. The crystalline size of the powders was evaluated based on X-ray diffraction measurements (XRD) performed using the Philips Analytical X'PERT PW-3710 equipped with an adapter for a low angular geometry GID. The specific surface area of the samples was determined by the BET method using nitrogen adsorption-desorption isotherms with ASAP 2010 Micrometrics. The particle size distribution (DLS) was characterized by a laser method employing the Malvern MasterSizer 2000.

2.2 Catalytic measurements

A fixed-bed, quartz flow reactor connected to a quadrupole mass spectrometer (QMS, Thermostar QSD 300, BALZERS) was used in the performed catalytic tests. Before proper catalytic measurements, for each sample (0.3 g) a standardization procedure, consisting of keeping the sample in a helium atmosphere at a gas flow of $100 \text{ cm}^3 \text{ min}^{-1}$ for 30 min until reaching 500°C, was applied. After this treatment, the reactor was cooled down to room temperature and the used gas was changed to the target mixture.

The catalytic tests were carried out at a gas flow of $100 \text{ cm}^3 \text{ min}^{-1}$, in the temperature range of 50°C to 700°C, with a gas mixture containing 1000 ppm N_2O in He. For a more complete characterization, all catalytic measurements were performed three times for each sample. To characterize the catalytic activity in a more precise manner, the temperature at which the conversion of N_2O to O_2 and N_2 was 50% (T_{50}) and 90% (T_{90}), respectively, was determined.

3 Results

3.1 XRD

Figure 1 presents the XRD spectra of all samples before impregnation. The identified reflections are from the cobalt (II, III) oxide phase (ICDD 04-006-9070) and the cerium dioxide phase (ICDD 03-065-5923).

Figure 1. The XRD patterns of $Co_3O_4-CeO_2$ catalysts before impregnation.

In the XRD spectra, no other phase containing Co and/or Ce was observed. Similarly, in Figure 2 one can see reflections from all phases after the impregnation process. After impregnation, reflections were not detected

from any of the compounds containing potassium. The CeO_2 crystallite size, regardless of its content in the sample, was approximately the same in the case of all samples, reaching about 27 nm. The diffraction lines of Co_3O_4 were changed after the addition of CeO_2 . They were broadened.

Figure 2. The XRD patterns of Co_3O_4 - CeO_2 catalysts after impregnation.

Figure 3. The crystallite size for Co_3O_4 .

It was calculated that the crystalline size of the pure cobalt (II, III) oxide phase was 42 nm and after having added CeO_2 it was reduced to about 32 nm. No clear trend for a systematic decrease or increase in the size of the crystallite of cobalt oxide (II, III) was shown with increasing the content of CeO_2 .

3.2 BET

The specific surface area of catalysts was enlarged from $8.67 \text{ m}^2\text{g}^{-1}$ to $49.61 \text{ m}^2\text{g}^{-1}$ before impregnation and from $8.21 \text{ m}^2\text{g}^{-1}$ to $43.46 \text{ m}^2\text{g}^{-1}$ after impregnation respectively.

Figure 4. The specific surface area of catalysts.

Figure 4 presents the specific surface area of samples when increasing the CeO_2 content. When compared to cobalt oxide, a systematic development of the specific surface area (as indicated by the black line) was observed with increasing the content of cerium oxide. After impregnation, the specific surface area was reduced for each sample because of filling the pores with potassium.

Figure 5. The exemplary isotherm adsorption-desorption curves.

Figure 5 is a collection of graphs showing desorption and adsorption for samples Co1.0Ce and Co1.0Ce_K . It can be seen that as a result of impregnation the size of surface pores was similar and there was an almost unnoticeable change in the specific surface area. For the remaining samples, the hysteresis curve of adsorption-desorption resembled the results presented in Figure 5. The average adsorption pore diameter before impregnation was calculated at 13.2 nm and after impregnation at 13.0 nm. The hysteresis curve, according to the de Boer classification, indicates the type of pores which have an elongated, tubular shape. At the same time, the hysteresis loop of adsorption and desorption isotherms represents the case in which adsorption involves the formation of a multilayer adsorbate film according to the principles of a classical BET theory.

3.3 Particle size distribution

The particle size distribution with respect to the quantity and volume of the selected samples, before and after impregnation, is presented in Figure 6. The mean particle size determined on the basis of number of particles in the case of sample Co0.0Ce is 64.5 nm both before and after impregnation with potassium ions. For this sample, before impregnation, was determining particle size on the basis of volume distribution and there are three peaks when it comes to the maximum particle size, i.e. 120 nm, 10 μm and 180 microns. The presence of such substantial grains may indicate the formation of large agglomerates, which was confirmed by the SEM examination. A similar dependence was found in the case of the same sample after impregnation (Co0.0Ce_K), where the two marked peaks were observed for the particle size of about 130 nm and 90 microns, which is also connected with the formation of large agglomerates of powder.

Figure 6 shows the volume of grains as a percentage relative to the particle size for another sample, Co0.5Ce . The largest amount of particles (in terms of volume) is observed for the particle size range of approx. 590 nm to approx. 420 microns for the sample before and after impregnation. However, the grains larger than 600 nm are actually agglomerates which was confirmed by quantitative analysis and morphological SEM observations. The quantitative percentage of the samples

showed that for the majority of particles the size was in the 35-275 nm range. Such a marked difference between the analysis of the particle size distribution showed as a volume percentage and the quantitative percentage was noticed due to the presence of a few but large agglomerates in powder (e.g. over 10 microns). The particle size distribution of the powder with the highest content of CeO₂ (Co1.0Ce) does not differ from the previously described ones. A cumulative curve based on a number of particles for samples Co1.0Ce and Co1.0Ce_K shows that the average grain size in both cases was about 56 nm. For samples Co0.0Ce and Co0.0Ce_K it equalled 65 nm and 56 nm and for samples Co1.0Ce and Co1.0Ce_K it reached 56 nm and 64 nm respectively.

Figure 6. Grain distribution for selected samples.

The weighted average particle size was calculated and collected in Figure 7 based on the data obtained when analysing the particle size distribution for a number of particles.

Figure 7. The weighted average particle size for all samples.

It was observed that the higher the content of CeO₂, the larger the weighted average grain size that was calculated in relation to the measurements of the number

grains. These results coincide with the information obtained from the BET analysis.

3.4 SEM

The selected catalysts are shown in the micrographs collected in Figure 8. All grains have irregular shapes and form large agglomerates, measuring about a few microns. The shape of these agglomerates is the same for all samples, irrespective of whether the amount of CeO₂ is low (0.1 mol CeO₂) or high (1 mol CeO₂). The chemical analysis in terms of chemical composition showed no significant deviation from the assumed chemical composition, as shown in Table 2 and Table 3.

The average size of grains determined based on the images was about 0.12 µm. After impregnation, the shape and size of agglomerates did not change significantly. These observations are consistent with the data obtained from the analysis of the particle size distribution.

Figure 8. SEM images of catalysts.

3.5 Catalytic tests

The Co-Ce catalysts were active in N₂O decomposition, which is shown in Figure 9 and Figure 10. The N₂O conversion was negligible up to about 350°C for all samples. It was observed that the addition of cerium oxide, regardless of its quantity, always improves the catalytic properties of pure Co₃O₄. In addition, ceria oxide can stabilize metal oxide supports and modify the catalytic activity by changing the redox properties of metal oxides [22].

The temperature at which the system reaches the N₂O decomposition of 50% is on average lower than about

30°C for samples containing CeO₂. The same tendency is observed for the temperature determining the conversion of 90%. T₉₀ is lower for the samples containing CeO₂ and, at the same time, 60-80 Celsius degrees higher than T₅₀, as shown in Figure 11.

Figure 9. The N₂O conversion before impregnation.

Figure 10. The N₂O conversion before impregnation.

Figure 11. Temperatures for N₂O conversion of 50% and 90%.

After impregnation, a significant improvement in the catalytic properties of all analyzed samples was demonstrated. The temperatures at which complete conversion was achieved were shifted towards lower values, which is presented in Figure 10. The catalytic activity was improved to the biggest extent for the samples in the case of which the CeO₂/Co₃O₄ molar ratio was in the range of 0.4 to 0.7. Lowering

of the temperature at which the system reached the N₂O conversion of 50% was observed from approximately 130 to 210°C. The sample showing the best catalytic properties was Co_{0.4}Ce_K.

4. Summary

A series of Co-Ce oxides composites was characterized by the XRD, SEM-EDX, DLS and BET techniques. All analysed catalysts were tested for the low-temperature N₂O decomposition.

The results suggested that the addition of cerium oxide causes an increase in the specific surface and an improvement in the catalytic activity. The specific surface area of the catalysts obtained after impregnation was reduced by filling the pores with potassium. X-ray examination carried out for a series of catalysts obtained by the precipitation of CeO₂ on Co₃O₄ showed the presence of phases from CeO₂ and Co₃O₄ oxides only. The crystallite size calculated using the Scherrer equation showed that for an impregnation process the size reduction of the crystallite derived from the Co₃O₄ phase occurred in the case of all samples. The specific surface area was enlarged when increasing the CeO₂ content for all samples. It was also found that the micropores in powders have an elongated cylindrical shape. The addition of CeO₂ considerably lowered the temperature at which the system reached the conversion of 90%. To sum up, impregnation exerts the most significant impact on the improvement of the catalytic properties.

Acknowledgment

M. Rajska acknowledges the Statutory Project for Science (Grant for Young Scientists no.15.11.160.763) 2015 at the Department of Inorganic Chemistry, Faculty of Materials Science and Ceramics AGH UST.

This work has been partially financed as a research project no. DEC-2014/12/S/ST8/00582 from the resources assigned for science by National Science Centre (NCN, Poland) and partially financed by the National Centre for Research and Development (NCBR, Poland) under the project no. PBS3/A5/49/2015.

References

1. L. Xue, H. He, Ch. Liu, Ch. Zhang, B. Zhang, Environ. Sci. Technol. **43**, 890 (2009)
2. E.A. Davidson Environ. Res. Lett. **7**, 024005 (2012)
3. E.A. Davidson, D. Kanter Environ. Res. Lett. **9**, 105012 (2014)
4. U. Chellam, Z.P. Xu, H.C. Zeng, Chem. Mater. **12**, 650 (2000)
5. J. Pérez-Ramírez, F. Kapteijn, Appl. Catal. B **47**, 177 (2004)
6. Y. Wu, C. Dujardin, C. Lancelot, J.P. Dacquin, V.I. Parvulescu, M. Cabié, C.R. Henry, T. Neisius, P. Granger J. Catal. **328**, 236 (2015)
7. P. Granger, P. Esteves, S. Kieger, L. Navascues, G. Leclercq Appl. Catal. B **62**, 236 (2006)
8. J. Petryk, E. Kołakowska, Appl. Catal. B, **24**, 121 (2000)

9. E. Iwanek, K. Krawczyk, J. Petryk, J.W. Sobczak, Z. Kaszukur, Appl. Catal. B, **106**, 416 (2011)
10. E. Pachatouridou, E. Papista, A. Delimitis, M.A. Vasiliades, A.M. Efstathiou, M.D. Amiridis, O.S. Alexeev, D. Bloom, G.E. Marnellos, M. Konsolakis, E. Iliopoulou, Appl. Catal., B **187**, 259 (2016)
11. I.V. Yentekakis, G. Goula, P. Panagiotopoulou, S. Kampouri, M.J. Taylor, G. Kyriakou, R.M. Lambert Appl. Catal., B **192**, 357 (2016)
12. L. Obalová, M. Reli, J. Lang, V. Matějka, J. Kukutschová, K. Kočí, Catal. Today **209**, 170 (2013)
13. D. Pietrogiaconi, M.C. Campa, L.R. Carbone, S. Tuti, M. Occhiuzzi, Appl. Catal., B **187**, 218 (2016)
14. G. Grzybek, P. Stelmachowski, P. Indyka, M. Inger, M. Wilk, A. Kotarba, Z. Sojka, Catal. Today **257**, 93 (2015)
15. M. Inger, M. Wilk, M. Saramok, G. Grzybek, A. Grodzka, P. Stelmachowski, W. Makowski, A. Kotarba, Z. Sojka, Ind. Eng. Chem. Res. **53** (25), 10335 (2014)
16. G. Grzybek, P. Stelmachowski, S. Gudyka, P. Indyka, Z. Sojka, N. Guillén-Hurtado, V. Rico-Pérez, A. Bueno-López, A. Kotarba, Appl. Catal. B **180**, 622 (2016)
17. A. Bueno-López, I. Such-Basanez, C. Salinas-Martinez de Lecea, J. Catal. **244**, 102 (2006)
18. S. Suarez, M. Yates, F.J. Gil Liambias, J.A. Martin, P. Avila, J. Blanco, Stud. Sur. Sci. Catal. **143**, 111 (2000)
19. S. Imamura, J. Tadani, Y. Saito, Y. Okamoto, H. Jindai, C. Kaito, Appl. Catal. A **201**, 121 (2000)
20. W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka, Catal. Today **137**, 418 (2008)
21. L. Xue, Ch. Zhang, H. He, Y. Teraoka, Catal. Today **126**, 449 (2007)
22. L. Xue, Ch. Zhang, H. He, Y. Teraoka, Appl. Catal. B **75**, 167 (2007)
23. G. Maniak, P. Stelmachowski, A. Kotarba, Z. Sojka, V. Rico-Pérez, A. Bueno-López, Appl. Catal., B **136-137**, 302 (2013)
24. P. Legutko, W. Kaspera, T. Jakubek, P. Stelmachowski, A. Kotarba, Topic Catal., **56**, 745 (2013)
25. G. Zhang, Y. Guo, L. Lu, Z. Zhang, L. Wang, L. Zhou, J. Shao, Mat. Lett., **125**, 162 (2014)
26. L. Li, L. Song, H. Wang, Ch. Chen, Y. She, Y. Zhan, X. Lin, Q. Zheng, Int. J. Hydrogen Energy **36**, 8839 (2011)
27. M. Mazaheri, S.A. Hassanzadeh-Tabrizi, M. Aminzare, S.K. Sadrezaad, Ceramic Materials, **62**, 529 (2010)
28. F. Zasada, P. Stelmachowski, G. Maniak, J.-F. Paul, A. Kotarba, Z. Sojka, Catal. Lett. **127**, 126 (2009)