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Nanostructured Co–Ce-*O* systems for catalytic decomposition of N_2O

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ABSTRACT

Two series of nanostructured materials were obtained by the reverse microemulsion method. It was confirmed obtaining of the nanometric crystallites of Co-substituted ceria solid solutions up to 15 mol% of Co, while the reverse oxide system was biphase, even at so low content of CeO_2 as 1 mol%. The differences in pores structure of the both series were observed as well as the size of crystallites, however limited within nanometric range. The biphase materials showed higher catalytic activity than the solid solutions of Co in ceria phase, though this activity increased with Co content in CeO_2 phase.

1. Introduction

Recently, the environmental impact of nitrous oxide (N_2O) has attracted strong attention due to its contribution to global warming and ozone depletion in the Earth's upper atmosphere. N_2O is produced both by natural and anthropogenic sources. The latter include fossil fuel and biomass combustion, land cultivation and chemical processes in which nitric acid is manufactured or used as reactant. In order to control the N_2O emission in chemical processes, a number of studies has been focused on developing catalysts for nitrous oxide decomposition. Among them, systems containing Co_3O_4 spinel were found to be one of the most effective catalysts [e.g. 1,2]. The reaction mechanism over the cobalt spinel based catalysts is generally considered as a charge donation from the catalyst to the antibonding orbital of the N_2O molecule. Such donation results in weakening of the N—O bond in nitrous oxide and therefore acceleration of the rate of its decomposition [3]. It was reported that activity of the Co_3O_4 based catalysts depends on methods of their synthesis as well as the presence of the other components [4–11]. Shen et al. [4] reported an increase in the catalytic activity of Co_3O_4 spinel after its deposition on MgO support. Yan et al. [5] shown that partial replacement of Co^{2+} cations in Co_3O_4 by Ni^{2+}, Zn^{2+} or Mg^{2+} significantly improved catalytic activity of cobalt spinel in the process of N_2O decomposition. There is a lot of reports presenting high catalytic activity of cobalt containing catalysts obtained from hydrotalcite precursors. Obalová et al. [e.g. 6,7] showed that effective catalysts for nitrous oxide decomposition can be obtained from the Co–Mn–Al hydrotalcite-like precursors. Active catalysts were also obtained from Cu–Co–Mg–Al and Co–Mg–Al hydrotalcites, especially when calcination was performed at temperatures high enough to form the spinel phases [8]. It was also reported that alkali promoters, especially potassium, significantly improve activity of cobalt containing catalysts [e.g. 7–9]. Recently, CeO_2 was proposed as component activating Co_3O_4 spinel for catalytic decomposition of N_2O [9–11]. Xe et al. [9,10] have shown that the CeO_2–Co_3O_4 oxide systems are significantly more active comparing to pure Co_3O_4 spinel and the activation effect of cerium is related to modification of the redox properties of cobalt as well as preservation of the relatively high surface area of the catalysts (especially for the samples with low loading of cerium). On the other hand Iwanek et al. [11] described the redox properties CeO_2–Co_3O_4 oxide systems and propose optimal composition of the catalyst.

Parrez-Esclapez et al. [12] compared catalytic activity of rhodium deposited on CeO_2 and γ-Al_2O_3 supports and showed that ceria activated rhodium for N_2O decomposition more effectively than alumina. This effect is probably related to the redox properties of cerium oxide, for which the formation of the surface nitrate (bridged, monodentate, bidentate), nitrite and nitro groups has been reported [12]. Distribution and population of these species depended on the reaction temperature and composition of reaction mixture (presence or absence of oxygen). Authors suggest that surface ceria oxygen is involved in oxidation of N_2O into the surface

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nitrogenated species. Decomposition of such species results in the formation of vacant sites on ceria, by oxygen depletion, and filling up such vacant sites by N_2O oxygen.

Although this oxide system is very interesting for potential application in N_2O decomposition, the number of scientific reports related to this type of catalysts is rather limited. Up till now, the CeO_2–Co_3O_4 catalysts for N_2O decomposition were synthesized by co-precipitation (with K_2CO_3 or KOH as precipitants), impregnation, citrate and thermal (thermal decomposition of mixture of $Ce(NO_3)_3$ and $Co(NO_3)_2$) methods. It was shown that method used for the synthesis of CeO_2–Co_3O_4 oxide systems significantly differentiates their catalytic performance. Therefore, in this work, we applied another way for synthesis of CeO_2–Co_3O_4 oxide system. The reverse microemulsion method, guaranteeing the formation of nanocrystalline oxide materials, was used for the synthesis of two series of the samples, which were tested in the role of the catalysts for N_2O decomposition.

2. Experimental

Two series of nanostructured materials based on cerium and cobalt were obtained by the modified reverse microemulsion method. Our intention was to prepare CeO_2 oxide in which part of cerium cations is substituted by cobalt ions (Ce–Co-*X* series) and Co_3O_4 partially substituted by cerium cations (Co–Ce-*X* series), where *X* denotes ever mol% of the dopant (Co or Ce, respectively). The first stages of the synthesis were the same for both series of the samples. Two water-in-oil (w/o) microemulsions containing 22 wt.% of water phase, 48 wt.% of cyclohexane (POCh) as oil phase and 30 wt.% of the surfactant (Triton X-100, Aldrich) and co-surfactant (n-hexanol, Carl-Roth) with a weight ratio 2:1 were prepared. The appropriate mixtures of cerium ($Ce(NO_3)_3 \cdot 6H_2O$, Sigma–Aldrich) and cobalt ($Co(NO_3)_2 \cdot 6H_2O$, POCh) salts in the desired proportion were dissolved in water phase of the first microemulsion.

The second microemulsion contained a precipitating agent diluted in water phase: tetrapropylammonium hydroxide ($(CH_3CH_2CH_2)_4NOH_{aq}$, Sigma–Aldrich) for synthesis of Ce–Co-*X* series, and NaOH (POCh) for synthesis of Co–Ce-*X* series. The intended cobalt content in the Ce–Co-*X* series was in the range of 1–20 mol%, similarly as the cerium content in the Co–Ce-*X* series. The two appropriate w/o microemulsions were carefully put together and stirred at room temperature for 24 h with a constant flow of air. The resulting mixture was separated by centrifugation and washed several times with acetone providing a powder precursor. Finally, the obtained powder was calcined in a flow of air at 500 °C for 3 h (for series Ce–Co-*X*) or at 600 °C for 3 h (for series Co–Ce-*X*). The optimal conditions of the calcinations processes were determined by the thermal analysis methods coupled with evolved gas analysis (EGA-TGA/DTG/SDTA).

The crystal structure of the obtained materials was characterized by powder X-ray diffraction using a PW3710 Philips X'Pert (Cu K_α radiation, 0.154178 nm). The average crystallites size (D_{XRD}) was calculated using the Scherrer equation. For the CeO_2 crystallites the broadening of the following reflections (1 1 1), (2 0 0) and (2 2 0) was taken for the calculations, while in the case of Co_3O_4 the reflections (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (4 4 0) were used.

The chemical analyses of the samples from series Ce–Co-*X* were done by ICP-OES method (Perkin Elmer Optima 2100). Prior to the analysis, the samples were digested in a mixture (2:1) of concentrated nitric acid and perhydrol. For analysis, characteristic emission lines of 418.7 nm (for Ce) and 228.6 nm (for Co) were used.

The porosity and surface area of nanostructured Co–Ce-*O* materials were determined using ASAP 2010 (Micromeritics). The samples were outgassed at 350 °C for 12 h under vacuum, followed by the N_2 adsorption at −196 °C. Surface area was determined using the BET equation, whereas pore size distribution was derived from the adsorption–desorption isotherm. The total pore volume was determined by means of the total amount of adsorbed nitrogen at $p/p_0 = 0.98$. The average grains size D_{BET} was calculated using Eq. (1), on the assumption of the particle sphericity.

$$D_{BET} = \frac{6 \times 1000}{S \times d} \tag{1}$$

where *S* – BET surface area [m^2/g]; *d* – density (for the Co–Ce-*X* series, density of CeO_2 in the fluorite structure is equal 7.215 g/cm^3; for the Ce–Co-*X* series, the average density was calculated using the percentage contribution of both phases – $d_{CeO_2} = 7.215\,g/cm^3$ and $d_{Co_3O_4} = 6.110\,g/cm^3$).

Catalytic measurements of N_2O decomposition were performed in a fixed-bed quartz microreactor at atmospheric pressure and in the range of temperatures from 200 to 500 °C. The composition of outlet gas was analyzed on-line using QMS detector (RGA 200, Prevac). For each experiment 100 mg of a catalyst was placed on quartz wool in the reactor (6 mm i.d., l = 365 mm) and outgassed in a flow of pure helium (grade 5.0) at 415 °C. After cooling the reactor below 200 °C, the gas mixture containing 0.5 vol% N_2O and 4.5 vol% O_2 in He was fed into the reactor using mass flow controllers (Brooks). The total rate of gas flow was set at 50 ml/min and the temperature increase was 10 °C/min. The m/e signals characteristics of N_2O (44) and possible reaction products (N_2 – 28, O_2 – 32, NO – 30, NO_2 – 46) were analyzed.

3. Results and discussion

In the XRD patterns recorded for a Ce–Co-*X* series, the only reflections characteristic of fluorite-like structure were present up to Ce–Co-15 composition, what proves that cobalt ions were successfully substituted into CeO_2 structure forming a solid solution (Fig. 1a). For higher cobalt loading a slight trace of Co_3O_4 spinel phase was observed. The results of chemical analysis confirmed (Table 1) that the intended composition of the samples was attained with good accuracy. Calculated lattice constant for Co doped ceria system reveals only slight decrease with an increase of dopant concentration, weaker than would be expected according to Vegard's rule. This phenomena may be explained by a concurrent oxygen vacancies formation and Ce^{4+} reduction, facilitated by the dopant substitution. The similar behavior was observed for Cu doped ceria system [13]. In contrary, the XRD patterns (Fig. 1b) of the materials based on cobalt oxide doped with cerium (Co–Ce-*X* series) revealed the presence of two phases (CeO_2, Co_3O_4). The particular contribution of these phases correlates with the initial Co/Ce ratio used in the synthesis. Therefore, the cerium substitution into Co_3O_4 spinel lattice seems to be impossible, while the reverse substitution of Co into CeO_2 phase has been confirmed. This discrepancy may be related to differences in electrical charge, size and coordination of Co and Ce ions, though the decisive factor which should be taken into account is much faster nucleation of ceria phase precursor in comparison with the spinel phase precursor. However, the average crystallites diameters (D_{XRD}) determined from XRD measurements (Table 1) of all the obtained materials are nanometric, the average crystallite size of the samples from Ce–Co-*X* series varies from 5 to 6 nm with an exception of Ce–Co-20 sample showing average size about 10 nm. The crystallites of Co–Ce-*X* series are significantly larger. Those belongs to CeO_2 phase are between 11.6 and 14.2 nm, while the crystallites of Co_3O_4 spinel are in the range of 19.6–22.4 nm. Such large differences in the crystallites size of CeO_2 phase in these two series must be related to the competitive nucleation and growth processes.

Selected adsorption–desorption isotherms obtained for the nanostructured Ce–Co samples are presented in Fig. 2. Because