Preparation of LaNiO$_3$ perovskite by oxalate and carbonate precursor method for utilization as catalyst for high-temperature decomposition of N$_2$O

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Abstract

The mixed oxide LaNiO$_3$ with perovskite structure was prepared by two relatively new and unconventional methods including preparation and thermal decomposition of mixed metal oxalate or carbonate precursors. The intermediates were prepared by reaction in a highly concentrated suspension (paste). The thermal decomposition conditions of these intermediates were described and the final calcination temperatures were determined, which was done using thermal analysis methods and X-ray diffraction. During the decomposition of mixed carbonates, one-phase LaNiO$_3$ is produced directly, in case of decomposition of oxalates, a mixture of LaNiO$_3$ and La$_2$O$_3$ is produced due to the formation of La$_2$O$_2$CO$_3$ during the heating. Catalytic decomposition of nitrous oxide at high temperature (650 – 930 °C) and high loading (GHSV = 350 000 h^{-1}) has shown high LaNiO$_3$ activity, even at lower temperatures. The results were compared with the same compound obtained by co-precipitation and by solid state reaction. Methods of preparation based on decomposition of oxalate and carbonate intermediates lead to the preparation of materials with appropriate composition, morphology, specific surface and high catalytic activity.

Keywords

perovskite, LaNiO$_3$, N$_2$O decomposition, oxalate precursor method, carbonate precursor method, thermal decomposition, mixed metal oxides

Introduction

An important feature of the perovskite structure is the flexibility of the crystal structure. Partial substitution of each cation site by some foreign cations with different valences can produce an atypical valency state, for example unstable Co^{4+} or Ni^{3+}[1]. There are a number of laboratory procedures for preparing compounds with perovskite structure. Laboratory methods can be divided into methods at high temperatures (solid phase reactions, precursor combustion, etc.) and methods at low temperatures (precipitation, thermal degradation of precursors, sol-gel methods, etc.) [1-7].

Various mixed metal oxides with perovskite structure were utilized in many catalytic reactions, e.g. catalytic decomposition, reduction and oxidation of NO, complete oxidation of CO and CH_4, oxidative reforming of hydrocarbons, catalytic combustion of volatile organic compounds, soot oxidation, oxidation removal of organic dyes in aqueous solution and low-and high-temperature decomposition of N_2O [8-10]. The significance of N_2O removal arises from its long-term effect in the ozone layer as a greenhouse gas, 310 times worse than CO_2 [11,12]. The production of adipic and nitric acid are the main industrial sources of N_2O [13, 14]. Perovskites seem to be suitable materials for the demanding conditions of secondary level of N_2O decomposition in nitric acid plants [9, 15] due to their temperature stability and structural resistance up to 1 300 °C. The mixed La-Ni oxides, composed of $LaNiO_3$, NiO, and La_2O_3, supported on pre-treated cordierite ceramics were tested in catalytic decomposition of nitrous oxide (N_2O) in the temperature range of 250-450 °C and at GHSV of 24 000 h^{-1}. The authors [16] showed increase of catalytic activity at temperatures higher than 350 °C, reaching conversion of N_2O >80% in all cases at 450 °C. Substituted perovskite with their high oxygen mobility and appropriate temperature stability are promising materials for high temperature decomposition of nitrous oxide [15,17-19].

This work is focused to confirm the presumed use of $LaNiO_3$ perovskite as a catalyst for the high-temperature decomposition of nitrous oxide under condition of secondary level of nitric acid production immediately below Pt/Rh catalytic mesh in ammonia burner. The production of the catalyst in industrial scale requires simple preparation method guaranteeing catalytically active perovskite product. For this reason, various preparation procedures and their influence on the catalytic activity were tested.

Experimental
Synthesis of powder materials

$LaNiO_3$ was prepared by four laboratory preparation methods. Firstly by a well-known solid state reaction method between La_2O_3 (99.9%, Sigma-Aldrich, treated at 850 °C prior to use to eliminate products resulting from air storage) and $NiCO_3.2Ni(OH)_2.xH_2O$ (99.9%, Sigma-Aldrich, the starting material weights were adjusted according to the results of thermogravimetry). The calcination of the starting material mixture was carried out in two steps (2 x 900 °C, 6 h), the mixture was thoroughly mixed between the steps [20]. In the case of precipitation method, 0.04 M aqueous solution of $La(NO_3)_3.6H_2O$ (99.1%, Alfa Aesar) and 0.04 M solution of $Ni(NO_3)_2.6H_2O$ (99.0%, Acros Organics) were slowly mixed at pH = 11 ± 0.1. The pH was maintained at the selected value by the addition of NaOH solution. The calcination of the washed and dried intermediate product was carried out in an electric furnace at 700 °C for 2 hours [21]. The other two syntheses were based on preparation of intermediates (precursors) and their thermal decomposition. Mixed oxalate and carbonate intermediates were prepared by reaction in highly concentrated suspension by gradual co-precipitation. $La(NO_3)_3.6H_2O$ (99.1%, Alfa Aesar), $Ni(NO_3)_2.6H_2O$ (99.0%, Acros Organics) and $Na_2CO_3.10H_2O$ (100.3%, Lach-Ner), resp. $Na_2C_2O_4$ (99.6, Penta Chemicals) were used for precursor preparation. The mixtures of starting materials in the required molar ratio were treated in a mortar mill for 3x10 minutes. Sodium oxalate or sodium carbonate was used in 15% excess over the stoichiometric ratio. Polyethylene glycol (PEG 400, Merck) was used as wetting agent. The intermediates were washed out with water to remove soluble byproducts and then dried on air, calcined in an electric oven at 800 °C and 700 °C for 2 hours for oxalate and carbonate precursor, respectively [22].

Characterization of powders

The formation of the perovskite samples was followed by thermal analysis method using STA 449C Jupiter (Netzsch) with simultaneous registration of TG and DTA curves in combination with phase analysis [23]. The thermal analysis measurements were carried out in open ceramic crucibles in the air atmosphere, between 30 and 900 °C with temperature rise 10 °C/min. The phase composition of final products and any intermediates was studied by X-ray diffraction (XRD). The results were obtained by using the diffractometer MiniFlex600 (Rigaku) working in Brag-Brentano (θ/2θ) geometry with 1D D/teX Ultra silicon strip detector and Kβ filter. Diffraction data were collected from 10° to 60° 2θ angle, step size 0.02° and speed of data collection 10°/min. $CuK_{\alpha 1}$ (λ = 0.15418 nm) radiation was used for the angular range of 2θ < 35°, Cu $CuK_{\alpha 2}$ (λ = 0.15405 nm) radiation was used for the angular range of 2θ > 35°. The identification of individual phases was based on the matching of the obtained diffraction patterns with data contained in the JCPDS database.

Scanning electron microscopy (SEM) was used to study the morphology of final products. Measurements were performed on JSM-5500 LV (Jeol), accelerating voltage 20 kV, angle of impact of the electrons on the sample plane 90°, the image was created using secondary electrons.

The specific surface area (S_{BET}) was determined using volumetric adsorption system Nova 2200e (Quantachrome) at -196 °C by nitrogen absorption. The absorption isotherms were fitted using the Brunauer-Emmett-Teller (BET) method to determine the specific surface area.

Catalytic tests

The catalytic activity of $LaNiO_3$ perovskites was measured over catalysts in the form of grains with average dimensions of 0.45 mm in a quartz U-shaped fixed-bed reactor. The measurements were performed in decreasing mode in a temperature range of 900 to 650 °C with 50 °C step to eliminate the possible structural changes caused by heating in corrosion gas mixture [24]. The steady state values were obtained after 40 min stabilization at each temperature step from three independent measurements. The reaction mixture was composed of 1 000 ppm N_2O, 0.5% NO, 2% O_2, 10% H_2O, and He as a balance giving the total flow rate 350 cm^3 min^{-1}. The set of several mass-flow controllers (Aalborg) and a water vapour saturator was used for the mixing of reaction gas. The gas hour space velocity (GHSV) was ensured by using sample volume 0.06 cm^3. The content of N_2O, N_2, and O_2 at the reactor inlet and outlet was determined on an in-line connected a 6090 gas chromatograph (Hewlet Packard) with a Hysep column (packed column) removing water vapour. An HP-Plot Q column (30 m × 0.53 mm × 40 μm film thickness), a 5A molecular sieve (30 m × 0.53 mm × 25 μm film thickness), and a thermal conductivity detector (TCD) were used to separate N_2O, N_2 and O_2 and register of their concentrations. The reproducibility of the N_2O conversion results was ± 2 %. The mass balance of the converted N_2O and the produced N_2 and O_2 was proven during the experiment.

Results and discussion

Thermal decomposition of mixed La-Ni carbonates is characterized by only two endothermic peaks on DTA curve (Fig. 1). The first endothermic peak with the minimum at 168 °C is accompanied with loss of molecular water with corresponding weight loss of 12.8% from initial mass on the TG curve [25]. Continuous drop in sample weight begins at 250 °C and ends at 721 °C. Decomposition of carbonate precursor takes place in two steps, which is evident from the course of the TG curve in this temperature range. The presence of the nickel carbonate or lanthanum carbonate phase has not been proved by XRD. The decomposition of the La-Ni intermediate thus proceeds in two steps, or two intermediates with different ratios of metals are formed. The weight loss in the first step is 21.2%, in the second step is 3.4%. The decomposition in second step is accompanied with slight endothermic effect on DTA curve with the minimum at 629°C. The samples calcined at 700 °C contain only a single phase of $LaNiO_3$ (PDF 01-070-5757).
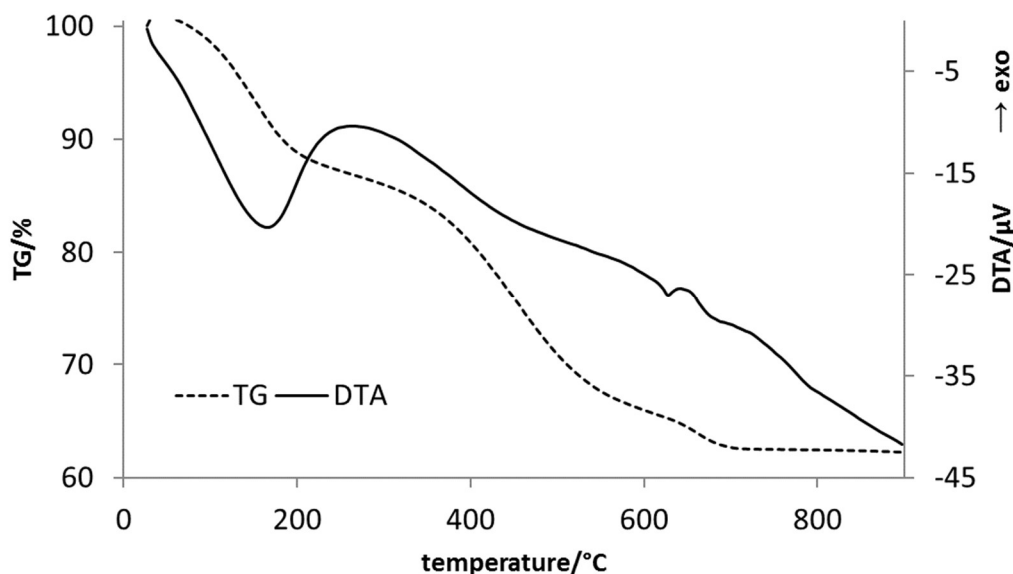
Fig. 1 DTA/TG curves of mixed lanthanum-nickel carbonate thermal decomposition for evaluation of calcination temperature for $LaNiO_3$ preparation (sample mass: 55.3 mg)

The single-phase intermediate of La-Ni oxalate did not form during the intermediate preparation. This was confirmed by XRD measurements and is also evident from the shape of the thermoanalytical curves (Fig. 2). The molecular water loss occurred in two steps during the thermal decomposition of La-Ni oxalate intermediate. The first step is accompanied with the minimum 166 °C on DTA curve and corresponding mass loss 6.8%, the second is accompanied with the minimum at 269°C and mass loss 7.5%. Endothermic peak on DTA curve with the minimum at 366°C corresponds to partial decomposition of La-Ni oxalate precursor and formation of carbonate

intermediate [26, 27]. Besides mixed carbonates, $La_2O_2CO_3$ (PDF 01-084-1963) also forms. The compound $La_2O_2CO_3$ decomposition is noticeable on DTA curve, endothermic peak with minimum at 793 °C and mass loss 3.0%. The weight loss value did not correspond to the theoretical value for the decomposition of $La_2O_2CO_3$, which together with the results of the XRD analysis shows that most of La is incorporated in the mixed intermediate, which decomposes at a significantly lower temperature (endothermic peak on DTA curve with minimum at 507 °C, mass loss 16.7%). Finally, the samples calcined at 800 °C contain phases of $LaNiO_3$ (PDF 01-070-5757) and La_2O_3 (PDF 01-074-2430).
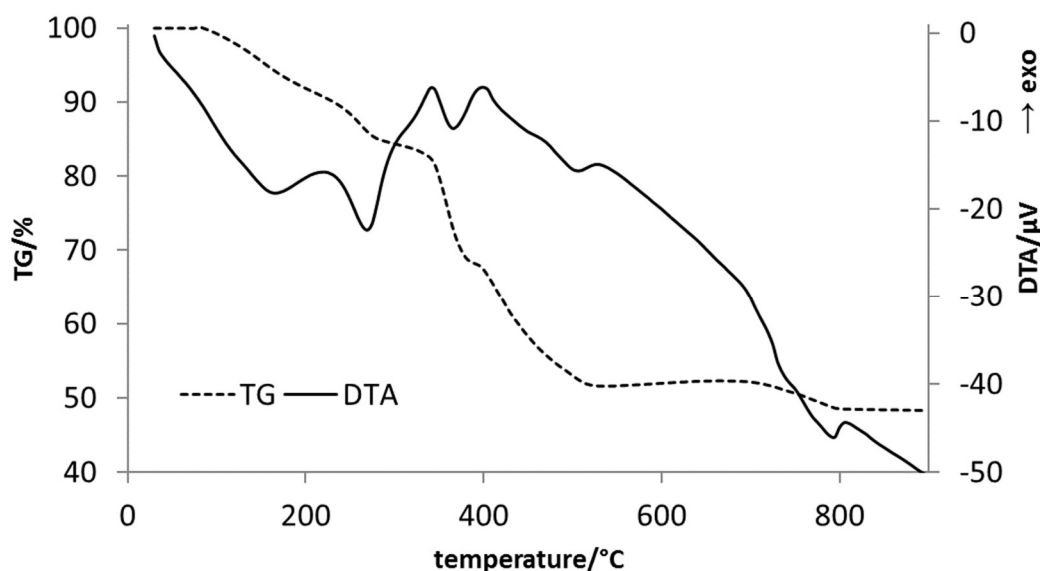

Fig. 2 DTA/TG curves of mixed lanthanum-nickel oxalate thermal decomposition for evaluation of calcination temperature for $LaNiO_3$ preparation (sample mass: 56.0 mg)

According to the results of the XRD analysis, the solid-state reaction failed to produce the expected compound. Repeatedly, a mixture of $La_3Ni_2O_7$ (PDF 01-070-5842) with perovskite structure and La_2NiO_4 (PDF 01-076-9302) with a spinel structure was obtained. The co-precipitation method with subsequent calcination leads to single phase sample of $LaNiO_3$ (PDF 01-070-5757).

The method of $LaNiO_3$ preparation strongly influences the morphology of prepared samples (Fig. 3). Sample prepared by the solid-state reaction method (A) has the character of compact particles with approximately uniform particle size distributions. Particles of irregular shape with the size of ones micrometres are in this case connected to larger units. Samples prepared by the solid-state reaction method have a specific surface area 1.2 m^2/g. In the samples prepared by decomposition of mixed oxalates (B) and carbonates (C) the plate-shape particles are present in higher concentration in the case of oxalate precursor. This type of particles is accompanied by submicron particles of irregular shape. Plate-shape particles caused errors in particle size evaluation by laser diffraction, therefore these results are not published in this contribution. The sample prepared by the thermal decomposition of oxalate intermediate method has a specific surface area 3.6 m^2/g, by the thermal decomposition of carbonate intermediate method 15.8 m^2/g.

Preparation by precipitation followed by calcination (D) leads to relatively large compact particles composed of small submicron particles with specific surface area 7.1 m^2/g.

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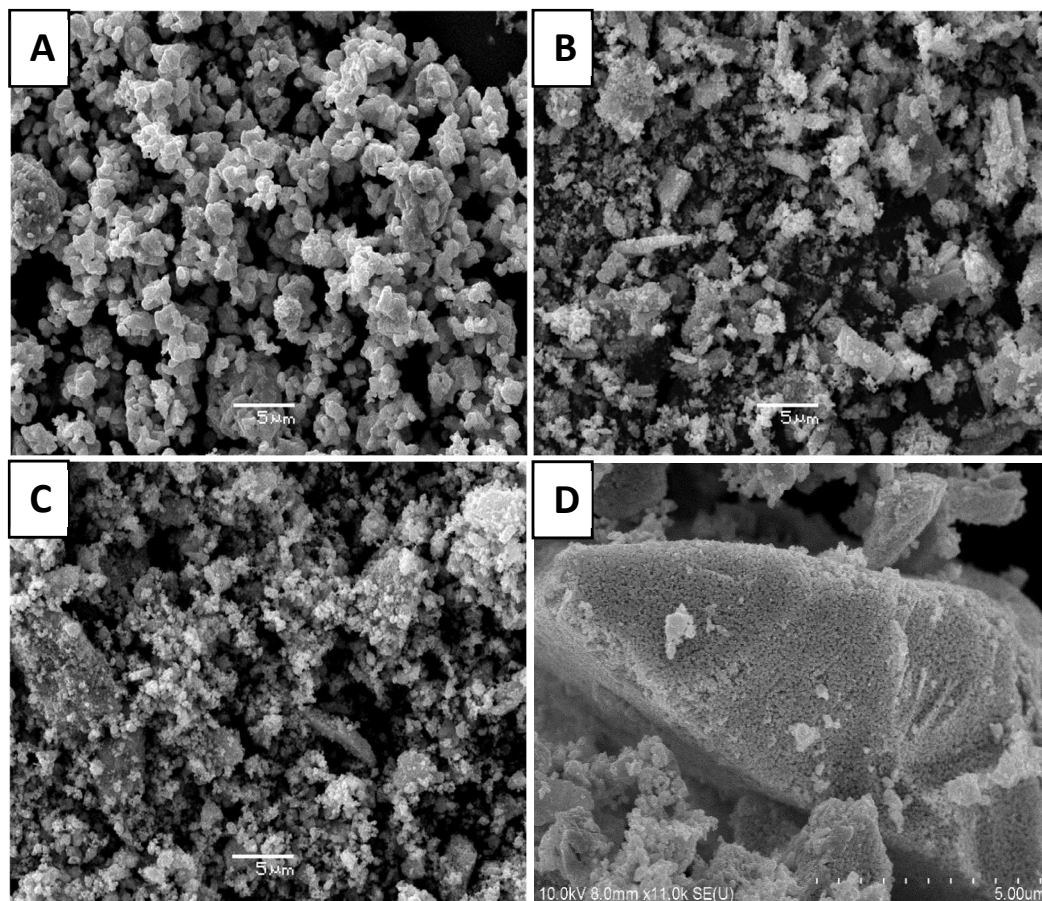
Fig. 3 SEM images of LaNiO$_3$ prepared by solid state reaction (**A**), LaNiO$_3$ prepared by thermal decomposition of oxalate intermediate (**B**), LaNiO$_3$ prepared by thermal decomposition of carbonate intermediate (**C**), LaNiO$_3$ prepared by precipitation with subsequent calcination (**D**)

Catalytic tests were performed at conditions identical to the nitric acid production, i.e. high temperature, high content of NO and water vapour. The GHSV usual in industry about 100 000 h^{-1} was not usable because of slight differences in N$_2$O conversion of all samples in experimental temperature range. Only the use of GHSV 350 000 h^{-1} allowed to distinguish the catalytic activity of differently prepared LaNiO$_3$ as is shown in Fig. 4. The catalysts prepared by thermal decomposition of oxalates (B) and carbonates (C) and by co-precipitation (D) were significantly more active than prepared by solid state reaction (A). Above this fact, the perovskites prepared with use of sodium oxalate or sodium carbonate (B and C) showed similar activity slightly higher than sample D in the lower temperature region. It is obvious that catalytic activity corresponds to morphology and specific surface area of prepared compounds. Sample prepared by solid state synthesis showed the lower value of specific surface area and as was mentioned above Ni is oxidized to Ni^{3+} only partially in this sample. The lower catalytic activity of sample prepared by co-precipitation at lower temperatures may be associated with partial inaccessibility of the particle surface (see Fig 3, D) because of large particle agglomerates.

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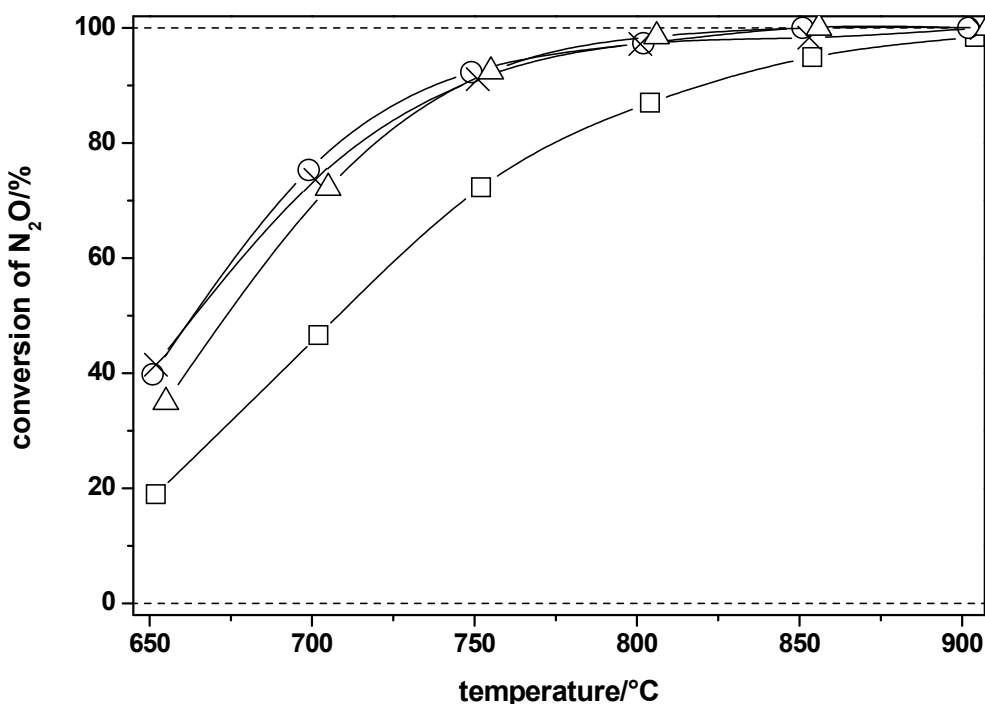
Fig. 4 High-temperature decomposition of N_2O over the $LaNiO_3$ perovskites prepared by different routes in gas mixture: 1 000 ppm N_2O, 0.5% NO, 2% O_2, 10% H_2O, and He. ($\square$ - A, $\bigcirc$ - B, $\times$ - C, and $\triangle$-D)

Conclusion

　　　　The La-Ni oxides with perovskite structure were produced by unusual method - thermal decomposition of oxalate and carbonate precursors prepared by reaction in highly concentrated suspension by gradual co-precipitation with oxalate and carbonate ion and by classical preparation methods; co-precipitation from solution and solid state reaction. The method of preparation by co-precipitation from solution and decomposition of metal carbonate intermediates leads to formation of a one-phase system - $LaNiO_3$. The particle material preparation method revealed differences in morphology where samples prepared by decomposing the precursors have plate-shape particles accompanied by small irregular particles and exhibit higher specific surface area. All prepared perovskites were used as a catalyst for high-temperature decomposition of N_2O under real conditions. The preparation route of the perovskite structure is influencing catalytic activity. The lowest catalytic activity is represented by a sample prepared by a solid-state reaction which exhibits compact particles with low specific surface area and an inappropriate phase composition, when Ni is only partially in oxidation state 3+. Mixed metal oxalate and carbonate precursors prepared by the novel gradual co-precipitation method proved to be a simple method for synthesis of perovskite compounds especially when requirements for specific surface properties and morphology are laid down.

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