

Cobalt-lanthanum catalyst precursors for ammonia synthesis: determination of calcination temperature and storage conditions

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A thermal decomposition of a cobalt-lanthanum catalyst precursor containing a mixture of cobalt and lanthanum compounds obtained by co-precipitation were studied using thermal analysis coupled with mass spectrometry (TG-MS). Studies revealed that the calcination in air at 500°C is sufficient to transform the obtained cobalt precipitate into Co_3O_4 , but it leads to only partial decomposition of lanthanum precipitate. In order to obtain Co/La catalyst precursor containing La_2O_3 the calcination in air at the temperature about 800°C is required. However, it is unfavorable from the point of view of textural properties of the catalyst precursor. A strong effect of storage conditions on the phase composition of the studied cobalt-lanthanum catalyst precursor, caused by the formation of lanthanum hydroxide and lanthanum carbonates from La_2O_3 when contacting with air, was observed.

Keywords: ammonia synthesis, catalyst precursor, cobalt, lanthanum, thermal analysis.

INTRODUCTION

In the literature cobalt catalysts are known as active systems for low-temperature NH_3 synthesis process^{1–9}, in particular when they are promoted with barium^{3–5} or selected rare earth metals (cerium^{6, 7} or lanthanum^{8, 9}). However, a preparation and subsequent application of catalytic materials containing lanthanum require a special attention. Lanthanum oxide exhibits a strong tendency to interact with H_2O and CO_2 present in air, which may have a significant impact on the phase composition and properties of La_2O_3 ¹⁰ and consequently also on the properties of the catalyst containing lanthanum oxide as an important component. A preparation method used (a type of lanthanum oxide precursor and its decomposition conditions)^{10–17} is also of great significance in this case. Hence, two important issues are necessary to be considered during a development of catalytic systems with lanthanum oxide. Firstly, a temperature of catalyst precursor calcination – it should be selected properly in order to obtain a material containing desired components and having optimal textural properties at the same time. Secondly, a possible change of a catalytic material composition caused by the interaction of La_2O_3 with H_2O and CO_2 contained in air, what can significantly modify final properties of the studied catalyst.

Because of its wide application potential thermal analysis is a useful tool in the investigation of properties of catalytic materials^{18–21}. In our previous paper²² it has been successfully applied to determine the composition of catalyst precursors containing cobalt and cerium or cobalt and lanthanum. Moreover, it is possible to simulate industrial operation conditions of catalysts (high temperature, atmosphere of various composition and properties – oxidizing, reducing) in a furnace of a thermobalance. This allows studies of many crucial catalyst properties, e.g. a course of catalyst reduction^{6–9, 23} or methanation process of activated carbons⁵ used as a catalyst support.

In the present work we used a thermal analysis coupled with mass spectrometry (TG-MS) to determine the appropriate calcination temperature of cobalt-lanthanum catalyst precursor obtained by co-precipitation and indicate the influence of conditions, in which such

a catalytic material is stored, on its composition. These are essential information, both from the point of view of future practical use of catalysts containing lanthanum oxide and precise analysis of their characterization studies results, in particular those carried out using ex situ techniques.

EXPERIMENTAL DETAILS

Preparation of catalysts precursors

A precipitate containing cobalt compounds, a precipitate containing lanthanum compounds and a co-precipitated mixture of cobalt and lanthanum compounds in fixed proportions were obtained by precipitation/co-precipitation⁸, respectively, using K_2CO_3 as the precipitating agent. An appropriate amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water and warmed to approximately 90°C. Then, a warm solution of K_2CO_3 was slowly added. The obtained precipitates were filtered under reduced pressure (about 0.04 MPa), washed with cold distilled water until pH was neutral and dried (120°C, overnight). For the calcination studies the precipitates as-prepared were used. While for the storage condition studies the co-precipitated mixture containing cobalt and lanthanum compounds was calcined at 500°C (Co/La(7.4) sample) and then divided into two parts. One of them was stored in a close vessel for 8 months. The second part of the sample was stored in an open vessel for 8 months in the contact with air. All the obtained materials and their pretreatment conditions are listed in Table 1.

EXPERIMENTAL METHODS

Thermogravimetric studies were performed using Netzsch STA449C thermobalance equipped with a quadrupole mass spectrometer Netzsch QMS 403C. Two types of experiments were conducted (Table 1):

Experiment 1 – the precipitate containing cobalt compounds, the precipitate containing lanthanum compounds and the co-precipitated mixture of cobalt and

Table 1. Experimental conditions and materials used for TG-MS measurements

	Material used	Pretreatment conditions	Type of TG-MS experiment
Calcination studies	precipitate containing Co compounds	as-prepared	<u>Experiment 1</u> 90% air/argon flow 100 mL/min heating rate: 10°/min heating to 500°C → isotherm 500°C (1 h) → heating to 800°C → isotherm 800°C (1 h) → heating to 1100°C
	precipitate containing La compounds	as-prepared	
	co-precipitated mixture containing Co and La compounds	as-prepared	
Storage conditions studies	Co/La(7.4) ^a	calcined at 500°C (16 h) in air (the reference material)	<u>Experiment 2</u> argon flow 100 mL/min heating rate: 10°/min heating from room temperature to 1100°C
		calcined at 500°C (16 h) in air, stored in a closed vessel (8 months)	
		calcined at 500°C (16h) in air, stored in an open vessel in the contact with air (8 months)	

^a La content (7.4 wt.%) determined by inductively coupled plasma optical emission spectroscopy (ICP-OES)

lanthanum compounds were heated gradually from room temperature up to 1100°C at the constant rate of 10°C/min. The temperature was raised to 500°C and then maintained for 1 hour (isothermal step 1). In the next step the temperature was increased to 800°C and maintained for 1 hour (isothermal step 2). In a final step the sample was heated to 1100°C. The system was supplied with 90% air/Ar mixture (flow 100 mL/min). The mass change, temperature and selected m/e signals (H₂O, CO₂, CO, NO, NO₂) were monitored throughout the entire measurement.

Experiment 2 – samples of cobalt-lanthanum catalyst precursor Co/La(7.4) (i.e. the material obtained after calcination of the co-precipitated mixture of cobalt and lanthanum compounds in air at 500°C), differing in the storage method (in a close vessel for 8 months from a preparation or in an open vessel for 8 months from a preparation) were heated from room temperature up to 1100°C at the constant rate of 10°C/min in a pure (≥ 99.999 vol%) argon constant flow (100 mL/min). The mass change, temperature, H₂O and CO₂ mass signals were monitored. The measurement was performed also for the studied cobalt-lanthanum catalyst precursor Co/La(7.4) immediately after preparation (the reference material).

During all experiments samples of approximately 15 mg were used. The reference crucible was empty. In order to avoid water physisorption all the necessary apparatus parts were kept heated to 250°C. The data analysis was carried out using Proteus Software (Netzsch).

A phase composition of the samples obtained (i.e. precipitates prior to heat treatment, as well as the precipitate containing La compounds after calcination in air (500°C or 800°C) were determined using X-ray powder diffraction studies. Data were collected with a Rigaku-Denki (Geigerflex) diffractometer in a Bragg-Brentano configuration using a Cu-sealed tube operating at 40 kV and 40 mA with the stability of 0.01%/8 hours. Measurements of each system were performed in the scattering 2θ range of 15° to 100° with a 0.02° step and a counting rate 6 s/step.

The textural parameters of the studied catalyst precursors were measured using a nitrogen physisorption technique with ASAP2020 instrument (Micromeritics). Prior to measurements samples were degassed (1 hour at 90°C and next 4 hours at 200°C). BET isotherm

equation was used to determine the total surface area, whereas the total pore volume was estimated based on BJH isotherm equation.

RESULTS AND DISCUSSION

Calcination studies

In order to determine the changes during calcination in air, the obtained precipitates were subjected to a thermal decomposition. Thermal analysis coupled with mass spectrometry allowed to simulate the real conditions during the calcination of the obtained samples in the furnace at temperatures up to 1100°C. However, the special attention was focused on the stages of annealing the samples at 500°C (isothermal step 1) and 800°C (isothermal step 2).

Figure 1 presents the results of the thermal decomposition of the precipitate containing cobalt compounds. In the initial step of a mass loss (about 100°C) a small

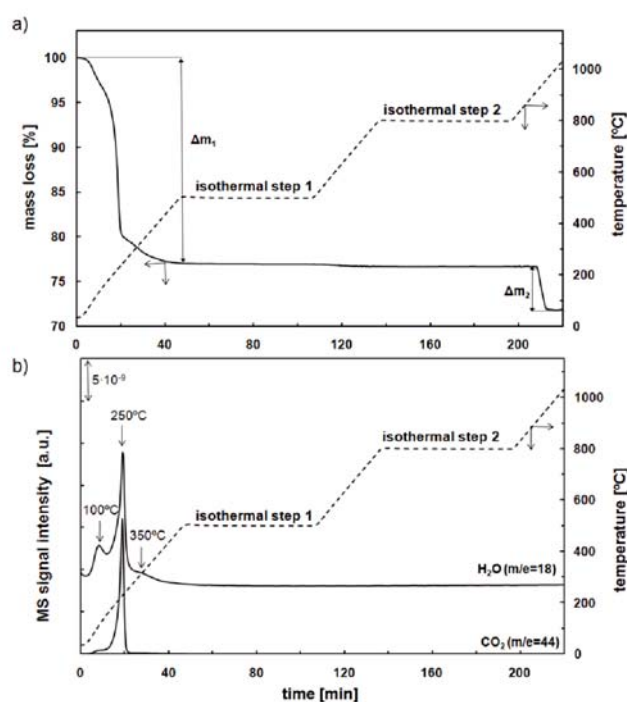


Figure 1. TG-MS calcination studies of the precipitate containing Co compounds: (a) mass loss, (b) mass signals of H₂O (m/e = 18) and CO₂ (m/e = 44)

peak on the mass signal of H₂O (*m/e* = 18) and a slight signal of CO₂ (*m/e* = 44) are visible, which correspond to desorption of water and carbon dioxide from the sample surface. With increasing temperature a significant mass loss (Δm_1), accompanied by the intensive peaks on H₂O and CO₂ mass signals with maxima at 250°C and 350°C, respectively, were observed. This indicates that during the precipitation process hydrated cobalt hydroxycarbonate of indefinite composition (Co_x(OH)_y(CO₃)_z · nH₂O) may be obtained, which is confirmed by the XRPD measurements results. In the diffraction pattern of the precipitated sample (Fig. 2) signals corresponding to Co(CO₃)_{0.5}(OH) · 0.11H₂O (JCPDS 48-0083) were observed. This phase decomposes to Co₃O₄ when temperature increases to 500°C. When the sample was annealed at 500°C (isothermal step 1), no mass loss on the TG curve, as well as no signals of released gases were recorded. Changes of TG curve did not occur also during further heating of the sample up to 800°C and its annealing at this temperature (isothermal step 2). The second mass loss (Δm_2), visible in the temperature range of 890–980°C, corresponds to the conversion of Co₃O₄ to CoO^{24, 25}, according to Eq. (1):



Further heating of this material up to 1100°C did not result in any other changes in the TG curve. The presented results clearly revealed that the calcination at 500°C is sufficient to transform the obtained hydrated cobalt hydroxycarbonate into cobalt oxide (Co₃O₄).

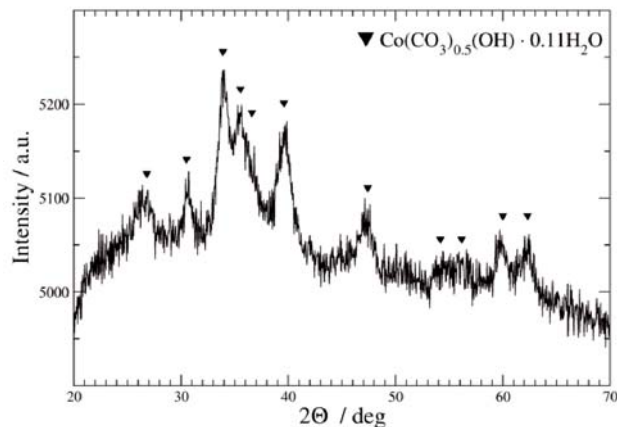


Figure 2. XRPD pattern of the precipitate containing Co compounds (prior to heat treatment)

The course of thermal decomposition of the obtained precipitate containing La compounds is presented in Figure 3. Initially a small peak on the mass signal of H₂O (*m/e* = 18) is visible, which corresponds to desorption of water from the sample surface. During heating the sample to the temperature of 500°C a substantial mass loss (Δm_1) was observed accompanied by intensive peaks on H₂O mass signals (with maxima at about 200°C, 350°C, 450°C) and CO₂ mass signals (with maxima at about 350°C, 450°C). This indicates that during the preparation process lanthanum carbonate hydrate (La₂(CO₃)₃ · xH₂O) and lanthanum carbonate hydroxide (LaCO₃OH) may be obtained. The presence of this later phase was indicated in the XRPD pattern (JCPDS 49-0981) – Figure 4. However, heating the sample to 500°C lead to its dehydration and dehydroxylation, visible as peaks on the *m/e* = 18

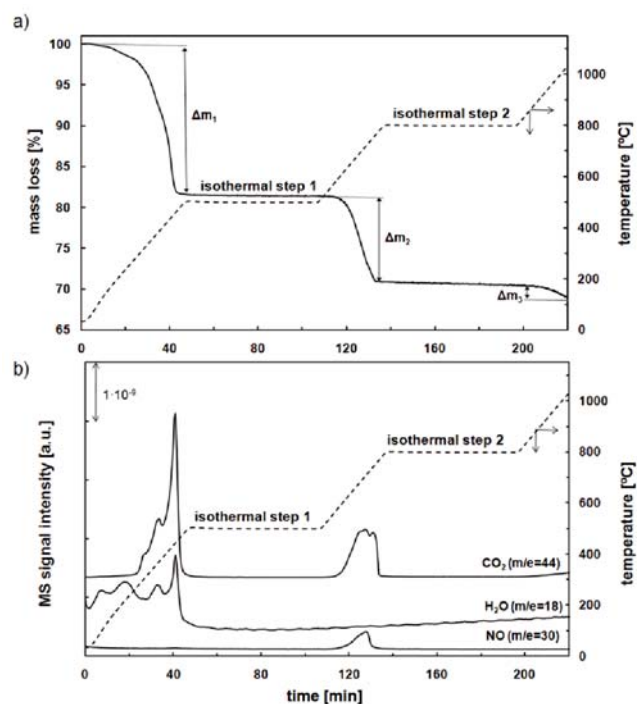


Figure 3. TG-MS calcination studies of the precipitate containing La compounds: (a) mass loss, (b) mass signals of H₂O (*m/e* = 18), CO₂ (*m/e* = 44) and NO (*m/e* = 30)

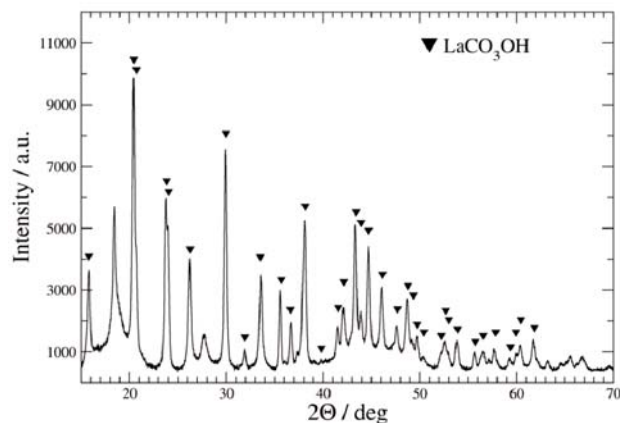
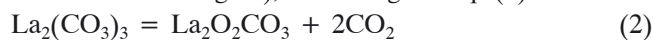


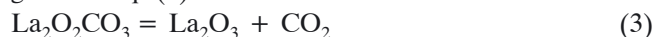
Figure 4. XRPD pattern of the precipitate containing La compounds (prior to heat treatment)

mass signal. The resulting lanthanum carbonate further decomposes to lanthanum dioxycarbonate (peaks on the *m/e* = 44 mass signal), according to Eq. (2):



This observation is confirmed by the diffraction pattern of the sample after its calcination at 500°C (Fig. 5), where signals derived from La₂O₂CO₃ phase are clearly visible. This is in good agreement with the literature^{10, 14}, which indicates that a thermal decomposition of lanthanum carbonate is a complex process and occurs with the formation of a stable intermediate product (La₂O₂CO₃). This compound, in turn, decomposes to lanthanum oxide at higher temperatures. During the conducted TG-MS experiment (Fig. 3) a decomposition of La₂O₂CO₃ to La₂O₃ occurred at two stages: when temperature increased in the range 500–800°C (the mass loss Δm_2 and the corresponding peak on the *m/e* = 44 mass signal were observed) and in the range of 800–1100°C, as it is confirmed by a small mass loss (Δm_3) and a slight raise

of the $m/e = 44$ mass signal (Fig. 3b). The decomposition of dioxycarbonate phase occurs according to the general Eq. (3):



Moreover, the observed mass loss ($\Delta m_2 + \Delta m_3$, about 12%) connected with the release of CO_2 corresponds well with the theoretical mass loss resulting from the Eq. (3). In addition, a small peak derived from NO ($m/e = 30$) was also visible at the temperature above 500°C . This is most likely the effect of a decomposition of lanthanum nitrate residues (in the form of LaONO_3)^{10, 26}, which was used during the precipitation process. Based on the presented results it can be stated that in order to obtain lanthanum oxide the calcination of the obtained lanthanum precipitate in air at temperature about 800°C is required. XRPD analysis (Fig. 5) confirms these observations – the diffraction pattern of the sample obtained after its calcination at 800°C indicates the presence of La_2O_3 phase only.

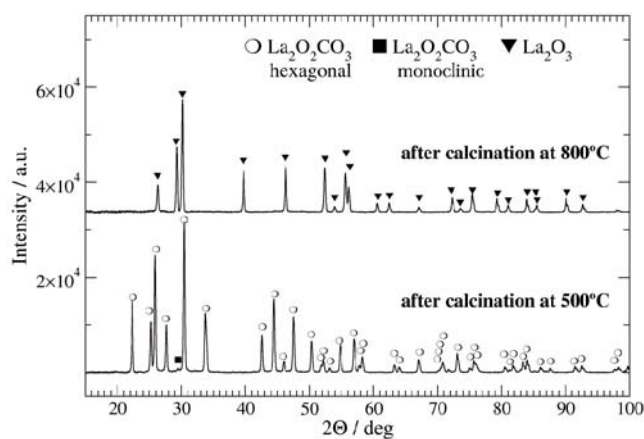


Figure 5. XRPD patterns of the precipitate containing La compounds after calcination in air at 500°C or 800°C

Due to a poorly organized (nearly amorphous) structure of the co-precipitated mixture containing Co and La compounds a determination of its phase composition by XRPD was impossible. Nevertheless, during the calcination of this sample – Figure 6, the same effects that were observed during the decomposition of the component materials, i.e. precipitate containing Co compound (Fig. 1) and precipitate containing La compound (Fig. 3), occurred. Three stages of decomposition of this mixture are clearly visible. The first stage (up to 500°C) with a mass loss Δm_1 and the evolution of H_2O ($m/e = 18$) and CO_2 ($m/e = 44$) is associated with a dehydration and decomposition of cobalt precipitate and a partial decomposition of lanthanum precipitate. The second stage (Δm_2 and a slight raise on the $m/e = 44$ signal) occurred in the temperature range of 500 – 800°C and is connected to a further decomposition of $\text{La}_2\text{O}_2\text{CO}_3$ to La_2O_3 . The last stage (Δm_3) at temperatures above 800°C is a result of $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ conversion, as described above.

Summing up this part of research it should be stated that a precursor of a cobalt-lanthanum catalyst obtained by calcination of a co-precipitated mixture of cobalt and lanthanum compounds at 500°C may consist of Co_3O_4 , La_2O_3 and $\text{La}_2\text{O}_2\text{CO}_3$. The formation of lanthanum cobaltite (LaCoO_3) is also possible as a result of the

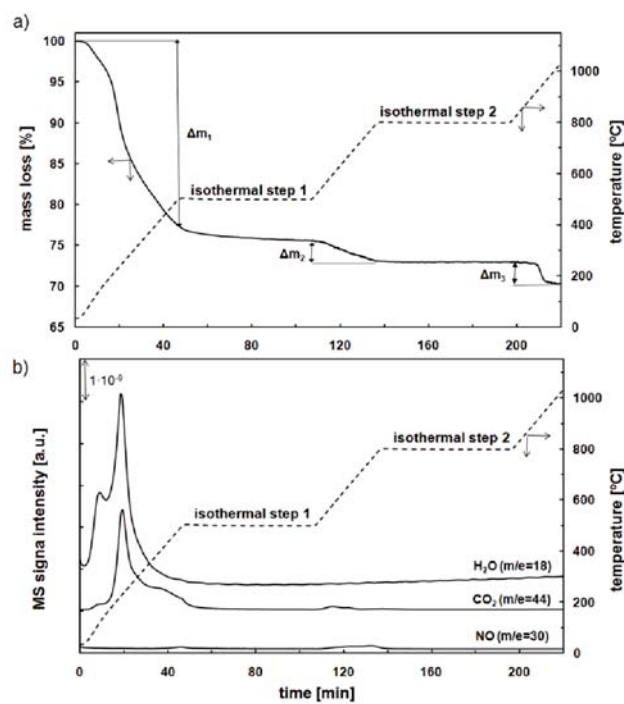


Figure 6. TG-MS calcination studies of the co-precipitated mixture containing Co and La compounds: (a) mass loss, (b) mass signals of H_2O ($m/e = 18$), CO_2 ($m/e = 44$) and NO ($m/e = 30$)

interaction of main components of the studied catalyst precursor under preparation conditions. This effect was observed in our previous studies of Co/La/Ba catalysts^{9, 28}. The diffraction patterns of the cobalt-lanthanum catalyst precursors presented in the paper⁹ clearly indicate that when the lanthanum content is properly high in relation to cobalt content, the LaCoO_3 phase is formed. The preparation of Co/La catalyst precursor containing Co_3O_4 and La_2O_3 oxides requires the use of higher calcination temperature (about 800°C). However, it is unfavorable from the point of view of textural properties of the catalyst precursor. In fact, high-temperature calcination led to an undesirable effect of lowering a surface area and porosity of a catalyst precursor (see Table 2), which may influence significantly properties of a final catalyst^{27, 28}.

Table 2. Textural parameters of the studied Co/La catalyst precursor after calcination at different temperatures

Calcination temperature [$^\circ\text{C}$]	Total surface area [m^2/g] ^a	Total pore volume [cm^3/g] ^b
500	51.7	0.26
800	3.2	0.01

^a total surface area determined on the basis of BET adsorption isotherm,

^b total pore volume determined on the basis of BJH adsorption isotherm.

The effect of storage conditions on the composition of the cobalt-lanthanum catalyst precursor

It is well known that lanthanum oxide is a highly hygroscopic compound and its easy interaction with H_2O and atmospheric CO_2 may affect significantly the phase composition of such a material (by creating hydroxides and carbonates)^{10, 11, 14}. Hence, storage conditions of lanthanum oxide are an essential factor influencing its properties and consequently the properties of catalysts, in which La_2O_3 is an important component. In order

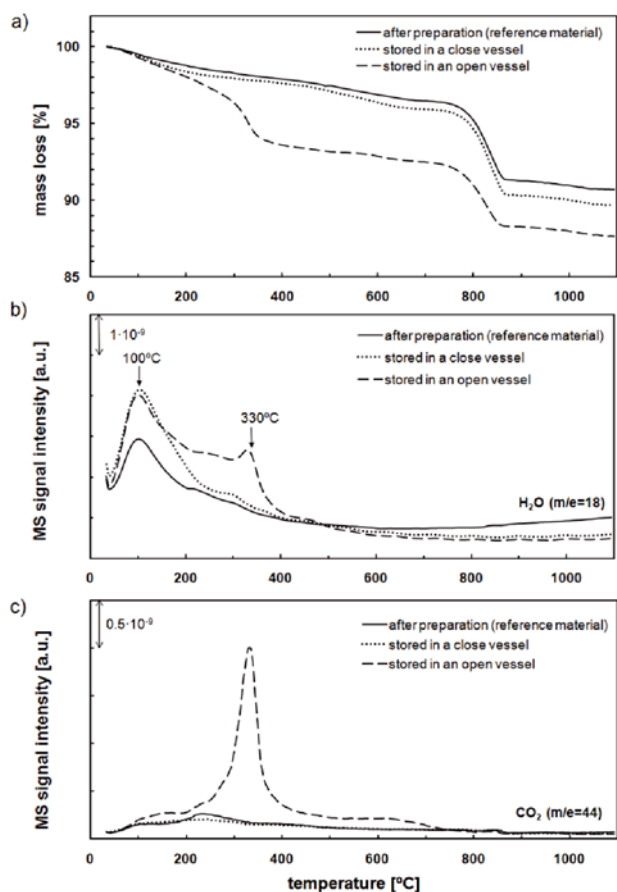


Figure 7. TG-MS studies of Co/La(7.4) catalyst precursor samples stored in different conditions: (a) mass loss, (b) mass signals of H₂O ($m/e = 18$), (c) mass signals of CO₂ ($m/e = 44$)

to determine the effect of the storage method on the composition of the cobalt-lanthanum catalyst precursor TG-MS studies were performed for Co/La(7.4) samples calcined at 500°C, but differing in storage conditions: in a close vessel for 8 months (after preparation) or in an open vessel for 8 months (after preparation). The obtained results were compared with those for the reference material, i.e. for the Co/La(7.4) catalyst precursor sample studied immediately after preparation (Fig. 7). For the reference material the initial slight mass loss (approx. 1.5%) was observed (Fig. 7a), associated with a H₂O desorption visible as a peak with a maximum at approx. 100°C on the $m/e = 18$ mass signal (Fig. 7b). For the material stored for 8 months in a close vessel a slightly larger initial mass loss (approx. 2%) appeared. It was accompanied by an increasing intensity of a signal of water desorbing from the sample surface at low temperatures (100°C). No pronounced signal of $m/e = 44$ was recorded (Fig. 7c) for these samples. For the material stored for 8 months in an open vessel (when contacting with air), the intensive desorption of H₂O was observed at temperature approx. 100°C. Moreover, the second peak of water occurred with a maximum at approx. 330°C. At this temperature a considerable amounts of CO₂ were released also, as reflected on the $m/e = 44$ mass signal as a large, sharp peak (Fig. 7c). It can be clearly seen that a storage of the cobalt-lanthanum catalyst precursor in a close vessel does not protect this material completely from exposure to ambient conditions. As a result, the sample adsorbed some amount of H₂O, as evidenced by an increase of the intensity of $m/e = 18$ signal. In turn,

a storage of the cobalt-lanthanum catalyst precursor in an open vessel caused a strong adsorption of H₂O and CO₂ from air. As mentioned above, the studied Co/La catalyst precursor (after calcination at 500°C) may contain a mixture of La₂O₃ and La₂O₂CO₃. These phases can easily react with water vapor and carbon dioxide from air. Binding of CO₂ by La₂O₃ causes the formation of carbonate forms^{10, 11, 14}, which then decompose during heating and give a clear peak on $m/e = 44$ mass signal (Fig. 7c). In turn, the interaction of La₂O₃ with H₂O leads to the formation of La(OH)₃ or LaO(OH) phases^{16, 29}, which decompose to lanthanum oxide at approx. 330°C, as indicated by the additional peak in the mass signal of water (Fig. 7b).

In conclusion, significant changes in the phase composition of cobalt-lanthanum catalyst precursors occur as a result of their contact with ambient conditions. It must be taken into account when these catalytic materials are in practical use. However, it is crucial particularly for the proper interpretation of results of catalyst characterization studies carried out using ex situ techniques.

CONCLUSIONS

In this study thermal analysis coupled with mass spectrometry (TG-MS) were applied to determine the course of the calcination process of a cobalt-lanthanum catalyst precursor containing a co-precipitated mixture of cobalt and lanthanum compounds. It was stated that the calcination in air at 500°C is sufficient to transform a precipitate containing Co compounds into Co₃O₄, but it does not lead to a complete decomposition of a precipitate containing La compounds. In order to obtain a cobalt-lanthanum catalyst precursor, containing Co₃O₄ and La₂O₃, a high-temperature calcination in air (about 800°C) of the obtained co-precipitated mixture is required. However, it causes a deterioration of textural parameters of a catalyst precursor. The storage method has a substantial effect on a composition of the studied Co/La catalyst precursor. The storage of this type of precursor in contact with air changes significantly its phase composition by a formation of lanthanum hydroxide and carbonates, which should be taken into account during application of these materials and analysis of their characterization studies results (ex situ measurements in particular).

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