

Properties and activity of the cobalt catalysts for NH₃ synthesis obtained by co-precipitation – the effect of lanthanum addition

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This article is dedicated to Professor Walerian Arabczyk on the occasion of his 70th birthday.

In modern research on catalysts for NH₃ synthesis a lot of attention is paid to cobalt. In this work the new catalytic systems based on cobalt are presented. Unsupported cobalt catalysts singly promoted (La or Ba) and doubly promoted (La and Ba) were prepared and tested in NH₃ synthesis reaction under commercial synthesis conditions. Characterization studies revealed that lanthanum plays a role of a structural promoter, which improves the surface of catalyst precursors and prevents from sintering during calcination. However, lanthanum has a negative effect on the reduction of cobalt oxide, but the addition of barium promoter (Co/La/Ba catalyst) diminishes the negative impact of La. The co-promotion of cobalt with lanthanum and barium results in the increasing of the active phase surface and improvement of its activity in NH₃ synthesis.

Keywords: ammonia synthesis, cobalt catalyst, promoter, lanthanum, co-precipitation.

INTRODUCTION

Although ammonia synthesis process is well-known for over one hundred years, there is still a need to make some changes in the technology aimed mainly towards reducing energy consumption¹. NH₃ synthesis is undoubtedly one of the most energy-consuming industrial processes¹⁻³. Difficult synthesis conditions significantly affect the energy consumption level, which consists of: preparation and compression of synthesis gas, NH₃ synthesis itself, compression of circulating gas and separation of the product¹. As a result, it consumes more than 1% of the energy generated in the world each year². In modern ammonia production plants the energy consumption index is about 30 GJ/t, whereas in the thirties of the twentieth century was 40 GJ/t and in the first Haber-Bosch factories in the early XX century was more than 90 GJ/t^{1, 4}. This indicates that a further reduction of energy consumption of process is still possible. The factor, which has the greatest influence on the energy consumption in NH₃ synthesis process, is pressure. There is not a shadow of doubt that the reduction of ammonia synthesis pressure (below 10 MPa) could be a very profitable solution and theoretically one of the ways to transform NH₃ synthesis into a more energy-efficient process. However, it requires a temperature decrease also and therefore the use of a new catalyst, which can operate efficiently and stable under lower pressure and in lower temperature⁵.

In modern studies of catalysts designed for ammonia synthesis a shift towards other metals, than previously used iron and ruthenium, is observed⁵. Numerous publications present new contacts for NH₃ synthesis containing cobalt⁶⁻²¹. Moreover, the addition of selected promoters to cobalt improves its ability to catalyze ammonia synthesis reaction^{6, 7, 18-20}.

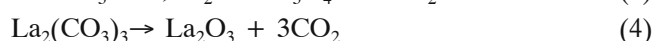
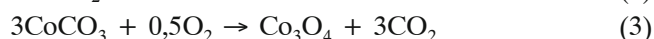
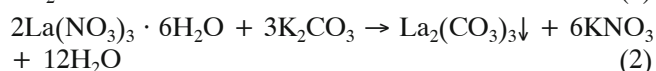
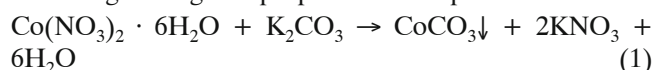
The aim of this work was the preparation of cobalt-based catalysts with the addition of a single promoter (lanthanum or barium) or two promoters (lanthanum and barium). The particular attention was focused on an estimation of the effect of lanthanum addition on

the physicochemical properties and activity of the tested catalysts in NH₃ synthesis. Moreover, the impact of lanthanum presence on the reduction of the catalyst was determined as an important stage of the preparation of catalytic systems for ammonia synthesis.

EXPERIMENTAL DETAILS

Preparation of catalysts

Preparation of the catalysts was based on the precipitation/co-precipitation described in our previous papers¹⁹⁻²¹. Cobalt carbonate was obtained by precipitation, whereas the mixture of cobalt and lanthanum carbonates was prepared by co-precipitation. Appropriate amounts of Co(NO₃)₂ · 6H₂O or a mixture of Co(NO₃)₂ · 6H₂O and La(NO₃)₃ · 6H₂O were dissolved in distilled water and warmed to approximately 90°C. Then, a warm solution of K₂CO₃ (precipitant) was slowly added. The obtained precipitates of cobalt carbonate or mixture of cobalt and lanthanum carbonates were filtered under reduced pressure and washed with distilled water to the pH about 7. The obtained materials were dried at 120°C overnight and calcined at 500°C overnight. Equations of reactions occurring during the preparation are presented below:



The obtained oxide materials were impregnated with an aqueous solution of promoter salt (Ba(NO₂)₂) using incipient wetness technique and dried at 120°C overnight. The final step of preparation was crushing and sieving the solid materials in order to get the 0.2–0.63 mm fraction. Symbols of the obtained catalysts are associated with the composition of their precursors, namely: Co/La – when a precursor was a mixture of cobalt and lanthanum oxides, Co/Ba – when a precursor consists of cobalt oxide

promoted with barium and Co/La/Ba – when a precursor consists of cobalt and lanthanum oxides promoted with barium. The chemical composition of the resulting materials is presented in Table 1.

Table 1. Chemical composition of the prepared catalysts

Catalyst symbol	Co content [wt.%]	La content [wt.%]	Ba content [mmol/g _{Co}]
Co/Ba	73.4	0	1.2
Co/La	59.3	7.4	0
Co/La/Ba	59.3	7.4	1.4

Characterization studies

The metallic cobalt content in the Co/La sample obtained by coprecipitation was determined by using thermogravimetric techniques (TG-MS), in which measurements in an inert and reducing atmosphere are coupled. The details of these experiments are described in our previous paper²². Lanthanum content was estimated by inductively coupled plasma optical emission spectroscopy (ICP-OES). The barium content in the impregnated materials (Co/Ba and Co/La/Ba) was determined based on the mass balance before and after an impregnation.

The physisorption measurements for all obtained catalysts precursors were performed by using ASAP 2020 equipment. Before the N₂ physisorption each sample was degassed at 90°C for 1 h and then at 200°C for next 4 h. The specific surface area (S_{BET}) was determined on the basis of BET isotherm equation, whereas the total pore volume (V_p) according to BJH isotherm equation. Additionally, physisorption characteristic was carried out for oxides: Co₃O₄ and La₂O₃.

The oxidized forms of samples, as well as the reduced materials (after catalytic tests) were characterized by X-ray powder diffraction (XRPD). Measurements were carried out at room temperature with a Siemens D 5000 diffractometer in a Bragg – Brentano configuration. Diffraction data were collected in the scattering 2θ range of 15–100° with a 0.02° step and a counting rate 10 s.

TPR-MS experiments were conducted using a NETZSCH STA 449C thermobalance equipped with a quadrupole mass spectrometer NETZSCH QMS Äeolos 403 C. Samples of approximately 15 mg were used. Catalysts precursors were heated to 550°C at the constant rate of 10°C/min in a H₂:Ar = 1:9 mixture (100 ml/min). Then the temperature and gaseous atmosphere were maintained for 2 h (isothermal segment). The mass change, temperature and selected m/z signals were monitored throughout the entire experiment. In order to avoid water physisorption all the necessary apparatus parts were kept heated to 280°C.

The H₂ chemisorption measurements (H₂-TPD) for studied cobalt catalysts were carried out in a fully automated PEAK4 instrument. In the first step catalysts samples were reduced at 550°C for 16 h in a H₂:Ar = 80:20 mixture (40 ml/min). After the flushing with Ar (40 ml/min) for 45 min and cooling to 150°C the H₂ chemisorption were carried out for 15 min under these conditions. Then, temperature was lowered to 0°C with a 20°C/min temperature ramp and H₂ sorption was continued under these conditions for 10 min. The sample was flushed with Ar to remove weakly adsorbed hydrogen. Next, the catalyst was heated in a argon constant flow (40 ml/min) with a 20°C/min temperature ramp and con-

centration of H₂ in the outlet gas was monitored (TCD detector). The obtained H₂ desorption profile allowed for the determination of H₂ amount desorbed from the Co surface. Consequently, the surface of the active phase was estimated. The H:Co_s = 1:1 stoichiometry²³ and the equation proposed by Borodziński i Bonarowska²⁴ were used for calculation.

Activity tests

The activity of the obtained catalysts were tested in ammonia synthesis reaction in a tubular flow reactor supplied with a pure (≥ 99.99995 vol.%) H₂:N₂ = 3:1 mixture ($x_1 = 0$). Under steady-state conditions of pressure (6.3 MPa), temperature (370–430°C) and gas flow rate (70.0 dm³[STP]/h) and for fixed catalyst mass (approximately 0.3 g_{Co}), the concentration of NH₃ in the outlet gas (x_2) was monitored – integral measurement. Before the catalytic tests, the samples were reduced in a stoichiometric H₂:N₂ stream under atmospheric pressure and at elevated temperature. The temperature program was as follows: 470°C (72 h) → 520°C (24 h) → 550°C (48 h).

RESULTS AND DISCUSSION

Catalysts characterization

The physisorption studies were carried out in order to determine the basic textural parameters (a specific surface area – S_{BET} and total pore volume – V_p) for studied catalysts precursors. The results for systems containing a mixture of cobalt oxide and lanthanum oxide (Co/La), cobalt oxide promoted with barium (Co/Ba) and a mixture of cobalt oxide and lanthanum oxide promoted with barium (Co/La/Ba) are presented in Table 2. Additionally, Co₃O₄ and La₂O₃ were also characterized.

Table 2. Textural parameters of the cobalt catalyst precursors and oxides: Co₃O₄ and La₂O₃

Catalyst symbol	S_{BET} [m ² /g] ^a	V_p [cm ³ /g] ^b
Co ₃ O ₄	42.9	0.298
Co/La	86.5	0.432
Co/Ba	28.3	–
Co/La/Ba	60.2	–
La ₂ O ₃	3.8	0.011

^a specific surface area determined on the basis of BET adsorption isotherm.

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

The obtained results indicate that specific surface area of cobalt oxide (42.9 m²/g) increased greatly as a result of the addition of lanthanum. For Co/La sample more than twofold increase in the specific surface area in relation to pure cobalt oxide was observed. For the materials impregnated with barium (Co/Ba and Co/La/Ba) S_{BET} decreased significantly compared to oxide materials without barium promoter. This is associated with the blocking of some pores as a result of crystallization of barium salt in the pores of oxide material. Lanthanum oxide, in turn, has a low surface area (3.8 m²/g) and thus a small volume of pores. Therefore, the porosity of this oxide is negligible, which confirms the pore volume distribution of the oxide materials investigated as a function of pore width (Fig. 1). For Co₃O₄ two distinct maxima at pore width of about 40 nm and

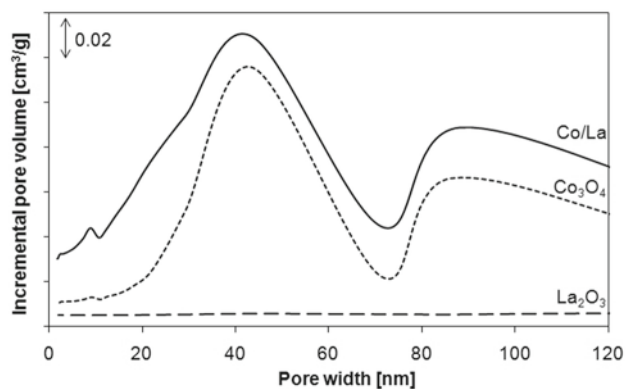


Figure 1. Pore volume distribution for the Co/La catalyst precursor and oxides: Co_3O_4 and La_2O_3

about 90 nm was observed. A pore distribution for system consisting cobalt and lanthanum oxides (Co/La) is quite similar to that for pure Co_3O_4 . Thus, mesopores and macropores have the largest contribution in the porosity of Co/La material.

Based on the textural results it can be concluded that a well-developed porous structure of the material containing cobalt and lanthanum (Co/La) is mainly due to the porosity of the basic component of the system, which is Co_3O_4 . The second component – La_2O_3 has no significant contribution in the porosity of the Co/La sample. However, an addition of lanthanum oxide, in the precipitation stage, has a very positive effect on the increasing of specific surface area (S_{BET}) of this material. In the studied systems lanthanum plays a role of structural promoter, which improves the surface of catalysts precursors and prevents a precursor from sintering during calcination.

The phase composition of the studied oxidized materials (prior to reduction), as well as in the reduced form (after catalytic tests) were determined using X-ray powder diffraction. The diffraction patterns are presented in Figure 2 and Figure 3, respectively. In all samples prior to reduction (Fig. 2) cobalt is in the form of Co_3O_4 . For the precursor based on cobalt and lanthanum oxides (Co/La) no signals from a lanthanum-containing phase have been detected. It may result from a relatively low lanthanum content in the sample (7.4 wt.%). It is also possible that La-based phase is present in the form of small crystallites or create a disordered structure, undetectable for XRPD. In the diffraction patterns of

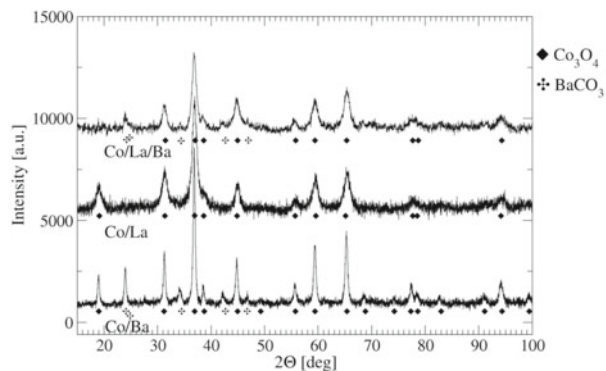


Figure 2. XRPD patterns of the catalyst precursors (prior to reduction)

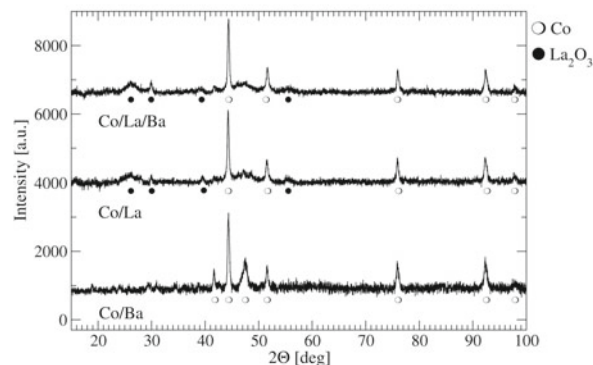


Figure 3. XRPD patterns of the catalysts after reduction (after catalytic tests)

samples promoted with barium (Co/Ba and Co/La/Ba), BaCO_3 phase has been observed. The presence of this phase may be caused by the transformation of barium precursor ($\text{Ba}(\text{NO}_2)_2$) taking place during preparation. The XRPD patterns of catalysts after reduction (Fig. 3) exhibit only signals derived from La_2O_3 and metallic cobalt. The lack of reflexes derived from Co_3O_4 phase is caused by its reduction to Co. No signals of barium-containing phases have been also detected, which may indicate that the barium precursor transform during the reduction in the form undetectable for XRPD.

The effect of lanthanum addition on the cobalt catalysts reduction

In order to determine the process of activation (reduction) of the studied promoted cobalt catalysts, the temperature-programmed reduction studies (TPR-MS) were carried out. The experimental results obtained for pure Co_3O_4 , cobalt oxide promoted with lanthanum (Co/La) and cobalt oxide promoted with lanthanum and barium (Co/La/Ba) are presented in Figure 4. The mass loss (Δm – TG curve) and MS signal of emitted water

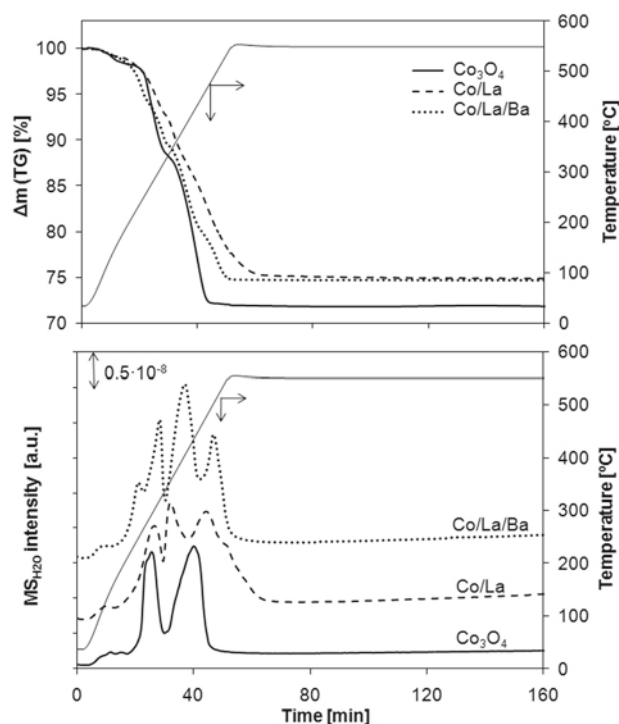


Figure 4. TPR-MS studies of cobalt oxide and the catalyst precursors: Co/La and Co/La/Ba

($m/z = 18$), as a major product of Co_3O_4 reduction, were observed. According to literature^{19–20, 25–30}, Co_3O_4 is reduced in two-step process, described by Eqs. (5) and (6):

$$\text{Co}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{CoO} + \text{H}_2\text{O} \quad (5)$$

$$3\text{CoO} + 3\text{H}_2 \rightarrow 3\text{Co} + 3\text{H}_2\text{O} \quad (6)$$

These reactions correspond to two visible mass losses on the TG curve for Co_3O_4 sample and two distinct $\text{MS}_{\text{H}_2\text{O}}$ signals with the maximum at 290°C ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ transition) and about 440°C ($\text{CoO} \rightarrow \text{Co}$ transition) – Figure 4. However, reduction of cobalt oxide ends during the increase of temperature (about 500°C) – polythermal segment. The presence of lanthanum in the Co/La sample causes a shift of the end of the reduction process in the direction of higher temperature (550°C). The reduction of the Co/La material lasts much longer and ends in the isothermal segment. Additionally, three mass losses on the TG curve were recorded, which correspond to the three signals on the $\text{MS}_{\text{H}_2\text{O}}$ curve ($T_{\text{max}} = 310^\circ\text{C}$, 360°C , 480°C). Even greater complication of MS signal of water has been observed for doubly promoted catalyst (Co/La/Ba), which clearly shows four signals corresponding to the four mass losses on the TG curve for the Co/La/Ba sample. In this case such complex course of reduction may be due to the presence of other phase containing Co – LaCoO_3 namely, which results from the interaction of sample components (Co and La). Although XRPD analysis showed no signals derived from this phase, its presence in this catalytic material can not be excluded. It is noteworthy that the reduction of the sample co-promoted with lanthanum and barium (Co/La/Ba) ends earlier than the reduction of the material promoted only with lanthanum (Co/La) – the maximum of $\text{MS}_{\text{H}_2\text{O}}$ peaks are slightly shifted towards lower temperatures and the process ends earlier, but still in the isothermal segment (at 550°C).

Summing up this part of research it should be stated that lanthanum has a negative effect on the cobalt oxide reduction process. In contrast, the additional introduction of the barium promoter (Co/La/Ba sample) gives the positive results – barium diminishes the negative impact of lanthanum on the reduction of this catalytic system. In our previous studies^{19–20} of promoted cobalt systems, a similar negative effect on the Co_3O_4 reduction was observed for other rare earth metal – cerium.

The effect of lanthanum addition on the active phase surface and its activity

In order to determine the surface of an active phase (metallic Co), the chemisorption experiments were conducted under the conditions, in which H_2 sorption occurred only on the surface of cobalt. As a result H_2 desorption curves (H_2 -TPD) were obtained. An example of H_2 desorption curve from the surface of the doubly promoted cobalt catalyst Co/La/Ba is shown in Figure 5.

Based on the amount of chemisorbed hydrogen and assuming a spherical model of the Co crystallites, the surface of the active phase (Co) available for hydrogen (S_{H_2}) was determined. S_{H_2} values determined for the studied promoted cobalt catalysts are presented in Table 3.

The S_{H_2} values vary depending on the composition of the studied material. Systems promoted with only one promoter (Co/La or Co/Ba) showed lower Co surfaces than doubly promoted systems (Co/La/Ba). The lowest

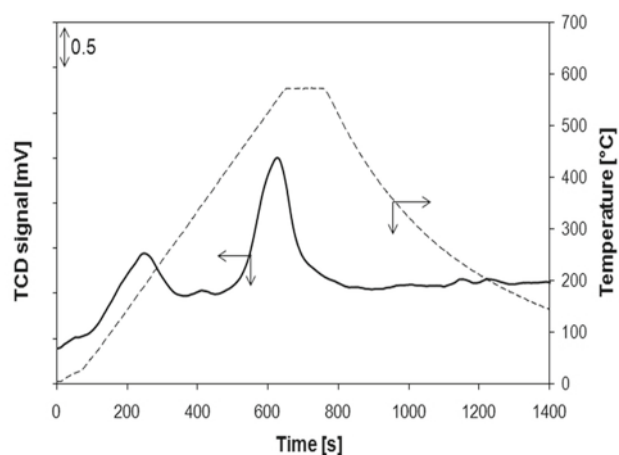


Figure 5. The H_2 desorption curve from the surface of the doubly promoted cobalt catalyst (Co/La/Ba)

Table 3. Surface of the active phase (S_{H_2}) and productivity of the promoted cobalt catalysts

Catalyst symbol	S_{H_2} [$\text{m}^2/\text{g}_{\text{Co}}$] ^a	Productivity [$\text{g}_{\text{NH}_3}/(\text{g}_{\text{Co}} \cdot \text{h})$] ^b		
		370°C	400°C	430°C
Co/La	2.2	0.01	0.02	0.03
Co/Ba	4.8	0.75	1.20	1.86
Co/La/Ba	8.7	1.41	2.19	3.27

^a S_{H_2} determined by H_2 chemisorption.

^b Conditions of activity tests in NH_3 synthesis reaction: $p = 6.3$ MPa, gas ($3\text{H}_2 + \text{N}_2$) flow rate = 70 dm^3 [STP]/h.

S_{H_2} value showed the cobalt catalyst promoted with lanthanum (Co/La) – 2.2 $\text{m}^2/\text{g}_{\text{Co}}$. It can be assumed that the addition of lanthanum may not be sufficient to prevent effectively from sintering of the active phase during reduction, although it improves successfully a specific surface area of the oxidized form of the catalyst (S_{BET}) – Table 2. The cobalt catalyst promoted with barium (Co/Ba) showed more than twofold higher Co surface than the system promoted with lanthanum (Co/La). This allows to conclude that barium interact strongly with the cobalt surface than lanthanum. The highest S_{H_2} value has been established for the doubly promoted cobalt system (Co/La/Ba). The active phase surface of this contact is about twice higher than the catalyst promoted only with barium (Co/Ba) and almost four times higher than the contact promoted only with lanthanum (Co/La).

Chemisorption data are in good agreement with the results of activity tests in NH_3 synthesis reaction (productivity – Table 3). The activity is strongly connected with the surface of the active phase. In all investigated temperatures the sequence of activity for studied catalysts is the same as for S_{H_2} values: Co/La/Ba > Co/Ba > Co/La. In the singly promoted systems barium acts better as an activator than lanthanum. In fact, the activity of the catalyst promoted only with lanthanum (Co/La) is negligible. However, the co-promotion of cobalt system with lanthanum and barium results in a significant increase in the activity of this contact. The doubly promoted catalyst (Co/La/Ba) is about twice more active than the system promoted only with barium (Co/Ba) and over two orders of magnitude more active than the catalyst promoted with lanthanum (Co/La). A beneficial effect of co-promotion of cobalt with lanthanum and barium, already observed during chemisorption measurements, is clearly visible also in the case of catalytic activity

(Table 3). Moreover, it is noteworthy that in the case of material containing both lanthanum and barium the synergic effect is observed. This means that the activity of the co-promoted catalyst is higher than the activity obtained after summing the values corresponding to catalysts with only one of these promoters. A similar effect occurred for the cobalt catalysts promoted with cerium and barium in our previous studies¹⁹.

CONCLUSIONS

Based on the obtained results it was found that lanthanum is an effective promoter of the cobalt catalyst for ammonia synthesis process. It plays a role of a structural promoter. The addition of lanthanum improves the textural parameters of the cobalt contact. The co-promotion of the cobalt catalyst with lanthanum and barium (Co/La/Ba) causes a significant increase of the active phase surface and the activity of the cobalt catalyst. However, lanthanum has a negative effect on the reduction of the cobalt catalyst. In the singly promoted systems (La or Ba) lanthanum is less effective as an activator than barium. Nevertheless, further studies are necessary to determine whether the increase of the La content will further improve the properties and activity of cobalt catalysts. Moreover, extensive studies are required also to establish the effect of activation conditions and prolonged treatment in H₂/N₂ mixture on the activity of the catalysts promoted with lanthanum and barium.

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