Synergistic Interaction of Cerium and Barium-New Insight into the Promotion Effect in Cobalt Systems for Ammonia Synthesis

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Abstract: This study explains a co-promoting interaction of cerium and barium additives in a cobalt catalyst used for ammonia synthesis. The results show that a synergistic effect of Ce and Ba promoters in the catalyst is associated with an emergence of a third promoter—BaCeO$_3$—which forms in situ from its individual components during catalyst activation. The influence of perovskite-type barium cerate is substantial due to its strong basic properties, i.e., high electron-donating ability and a tendency to stabilize the Co hcp cobalt phase (more active in ammonia synthesis than the Co fcc phase). BaCeO$_3$ diversifies the structure of adsorption sites on the cobalt surface by contributing to the exposure of facets with more favourable adsorption and binding energies with regards to rate-limiting reactions steps. It allows to a more fluent formation and transfer of species unrestricted by the hydrogen or product poisoning consequently accelerating the entire ammonia synthesis process.

Keywords: ammonia synthesis; cobalt catalyst; synergistic effect; cerium promoter; barium promoter; barium cerate

1. Introduction

Ammonia synthesis is a spectacular example of a heterogeneous catalytic process. Its enormous significance results not only from the fact of its developed, well-controlled and conducted for over a century production for the needs of large-scale fertilizers industry, but also due to numerous scientific aspects. The ammonia synthesis is a flagship reaction carried out in the presence of a catalyst. It seems particularly important that the studies of the catalysts of this process led to the definition of the phenomena and concepts essential for the whole field of catalysis, such as catalyst poisoning or promotion effect [1–5]. The latter is still of great interest to researchers from the point of view of ammonia synthesis catalysts development and many literature reports have shown its complexity and the multiplicity of effects caused by promoters [4,5] in relation to the active phase, catalyst supports or the interaction of its components. From the point of view of civilization development the further search for new ammonia synthesis catalysts facilitating its effective run under milder conditions of temperature and pressure is vital. Nowadays, research is focused on cobalt-based systems [6–14] which for the efficient operation require the application of properly selected promoters [9–14].
In heterogeneous catalysis it is sometimes observed that application of multiple promoters leads to significant, unexpected improvements in the performance of a catalyst. This phenomenon is called a synergistic effect of promoters. When it occurs, the catalytic properties of a system promoted with at least two compounds are much more favourable than would result from the properties of the sum of each individually promoted system component. This added value effect has been observed in various catalytic systems [11, 15–21]. For example, the co-action of Cu and K in the iron catalyst used for the CO$_2$ hydrogenation process [15], Na and S in the Fe-based catalyst used for Fischer-Tropsch synthesis [16, 17] or Zn and Ce in a bimetallic Co-Mn system for CO hydrogenation [18]. However, it is sometimes difficult to understand the interaction between individual promoters or promoters and metal in the active phase and to explain the synergistic effect. Our previous studies on cobalt catalysts used for ammonia synthesis also indicate the existence of the synergistic effect between cerium and barium promoters [11]. Although the specific properties of the co-promoted cobalt system have been already observed, the effect has not been explained to this day. Moreover, we consider the explanation to be equally important as the discovery itself. Basic results of the mentioned studies, i.e. the specific surface area of the active phase (metallic cobalt) and the activity of the catalysts expressed as an average reaction rate (productivity) and turnover frequency (TOF), are summarized in Table 1. All of the relevant physicochemical properties of the materials (e.g. a specific surface area of the unreduced and reduced forms, a surface area of the active phase and reducibility) are described in [11].

| Catalyst Symbol | Ce Content (mmol g$_{Co}$$^{-1}$) | Ba Content (mmol g$_{Co}$$^{-1}$) | Active Phase Surface (m$^2$ g$_{Co}$$^{-1}$)$^a$ | Productivity (gNH$_3$ g$_{Co}$$^{-1}$ h$^{-1}$)$^b$ | TOF (s$^{-1}$)$^c$ |
|-----------------|----------------------------------|-------------------------------|-----------------------------------|---------------------------------|-----------------|
| Co              | -                                | -                             | -                                 | -                              | 0.0004$^d$      |
| Co/Ce           | 1.0                              | -                             | 8.8                               | 0.39                            | 0.023           |
| Co/Ba           | -                                | 1.4                           | 4.1                               | 1.20                            | 0.103           |
| Co/Ce/Ba        | 1.0                              | 1.4                           | 9.8                               | 4.54                            | 0.238           |

$^a$ determined on the basis of hydrogen chemisorption studies (H$_2$-TPD experiments); $^b$ an average reaction rate under conditions: T = 400 °C, p = 6.3 MPa, H$_2$/N$_2$ = 3:1; $^c$ TOF (turnover frequency) estimated on the basis of the chemisorption data (H$_2$-TPD) and catalytic tests results; $^d$ [22].

It is clearly visible that the cobalt catalyst simultaneously promoted with cerium and barium (the Co/Ce/Ba sample) exhibits significantly higher activity in ammonia synthesis compared to the singly promoted systems. The TOF value for the Co/Ce/Ba sample is approx. 2–3 times higher than the value for the Co/Ba catalyst and over ten times higher than that for the Co/Ce (see Table 1). Cerium oxide is considered to be a structural promoter of cobalt [11, 12]. It prevents Co particles from sintering under the reaction conditions and contributes to stabilization of the metallic cobalt hcp phase which is more active in ammonia synthesis due to the higher intrinsic activity and higher density of active sites than on fcc Co, what has been proven both experimentally and through theoretical calculations [22, 23]. Moreover, cerium oxide can be used as a support for cobalt in the discussed reaction [10, 24, 25] and in water gas shift reaction as well [26, 27]. This is because of its unique redox properties and/or ceria’s ability to provide a higher metal dispersion. Barium is regarded as a promoter with mainly electronic character [28–31], but its structural influence is also observed [11, 32, 33]. Lee proves that Co/CoO$_2$ catalyst doped with barium is more stable in water-gas shift reaction (WGS) conditions than the unpromoted system, what results from its high sintering resistance [27]. Lin claims that Ba may affect the catalytic performance of Co/CoO$_2$ catalyst for ammonia synthesis by changing the adsorption performance of hydrogen and nitrogen, rather than its electronic properties [10]. However, the origin of cerium and barium synergistic cooperation had not yet been discussed.

In this work an attempt to explain the high activity of Ce and Ba co-promoted cobalt ammonia synthesis catalyst has been made. The research was carried out in such a manner to allow the analysis of the catalysts operation in their active form. Supplementary characterisation studies, i.e. the analysis
of materials phase and surface composition and their structure before and after reduction, the basicity and interaction with reaction reagents (H₂, N₂) was carried out. Results presented in this paper allowed us to determine the source of exceptionally beneficial properties of the doubly-promoted Co/Ce/Ba system for ammonia synthesis reaction in comparison to the singly-promoted cobalt systems (the Co/Ce and Co/Ba catalysts).

2. Results

2.1. X-ray Powder Diffraction (XRPD) Measurements

XRPD measurements were carried out for as-prepared samples (precursors) and for the reduced samples. In the Co/Ce sample before the reduction a cobalt oxide Co₃O₄ phase (ICDD No. 04-014-7752) is observed (Figure 1A). The diffraction lines characteristic for cerium oxide CeO₂ (ICDD No. 04-015-0471) are barely notable. Only detailed inspection of the positions of the most intense CeO₂ diffraction lines (at 28.6, 33.1 and 56.4°) proves the existence of weak and broad diffraction lines which can be attributed to CeO₂ phase. It is suggested that cerium oxide is well-dispersed or poorly organized in the sample. After the reduction of the precursor diffraction lines characteristic for cerium oxide (at 28.6, 33.1 and 56.4°) emerge notably, confirming the presence of CeO₂ phase in the reduced Co/Ce sample. The set of the most intense diffraction lines present in the XRD pattern after the reduction of that sample is ascribed to metallic Co fcc structure (ICDD No. 04-014-0167). A hcp phase of metallic Co (ICDD No. 04-015-9495) is also identified (notice peak at 41.3° and 47.1°). A hcp phase of metallic cobalt is not expected in the reduced Co/Ce sample, since an allotropic transformation of cobalt from hcp to fcc phase should occur at temperature near 420 °C [22,34]. However, it has already been reported that the addition of cerium oxide stabilizes the cobalt hcp phase up to the temperature of 600 °C [12,35]. It is worth noting that reflections attributed to the Co hcp phase are considered to originate from stacking faults of Co atoms. Nanocrystalline cobalt exhibits a tendency to create polytypic structure with high concentration of stacking faults [36]—their occurrence in the Co/Ce catalyst is confirmed by X-ray diffraction. In particular, the ratio of lines intensity in reflections attributed to fcc and hcp Co structures is inconsistent in comparison to standard patterns of respective phases. The stacking faults disorder in cobalt structure results in anisotropic peak broadening on the X-ray diffraction pattern [37]. Particularly noticeable is a relatively broad peak at 47.1°.

Figure 1. XRPD patterns of the Co/Ce (A), Co/Ba (B) and Co/Ce/Ba (C) samples before and after the reduction; data collected at ambient temperature and at reduction temperature (550 °C), respectively.
In case of the Co/Ba material in the unreduced form, two crystallographic phases were identified: cobalt oxide \( \text{Co}_3\text{O}_4 \) and barium carbonate \( \text{BaCO}_3 \) (ICDD No. 04-015-3216) (Figure 1B). The presence of barium carbonate may be a result of surface contamination with \( \text{CO}_2 \) during sample calcination in air. After the reduction metallic cobalt with (fcc) lattice was identified in the sample and barium carbonate was the only phase identified for barium compounds. \( \text{BaCO}_3 \) decomposes to \( \text{BaO} \) and \( \text{CO}_2 \) above 1300 °C, thus its occurrence in the material after reduction is justified [38].

The diffraction patterns of the Co/Ce/Ba sample are shown in Figure 1C. Only two phases, cobalt oxide \( \text{Co}_3\text{O}_4 \) and barium carbonate \( \text{BaCO}_3 \), were identified in the unreduced form of the sample. There are no reflections which can be attributed to the phases containing cerium element both before and after the Co/Ce/Ba sample reduction. It is supposed that cerium oxide is well-dispersed or it forms an amorphous phase as it was observed for the Co/Ce sample. The treatment at 550 °C under hydrogen/argon atmosphere results in a complete reduction of cobalt oxide. The diffraction lines characteristic for cubic (fcc) phase of metallic Co are observed together with these attributed to the hexagonal (hcp) Co phase. The profile of the diffraction lines ascribed to hcp Co phase located at 41.3 and 47.1° differs from the same lines observed for the Co/Ce sample. In case of the Co/Ce/Ba sample both lines are symmetrical and have similar width. The other phases identified in that sample are barium carbonate and cerium oxide which are also observed in the Co/Ba and Co/Ce samples, respectively. However, an additional crystallographic phase containing both barium and cerium, i.e., barium cerate \( \text{BaCeO}_3 \), is also identified (ICDD No. 04-015-3335). The presence of the phase has been previously noted in our cobalt catalytic systems promoted with Ce and Ba after the reduction [11–13,39].

Rietveld analysis was used for quantitative estimation of the Co/Ce, Co/Ba and Co/Ce/Ba catalyst composition. Results are listed in Table 2, where it can be seen that hcp phase of cobalt is found only in the Co/Ce/Ba and Co/Ce catalyst. While in the double promoted sample its presence is evident, in the latter it is less certain due to possible stacking faults or existence of polytypic phase. In the Co/Ce sample hcp phase stabilisation is attributed to cerium oxide and in the Co/Ce/Ba it is all probability connected with presence of \( \text{BaCeO}_3 \) perovskite phase. Moreover, it was calculated that in the Co/Ce/Ba sample the Co hcp dominates in quantity over the Co fcc phase.

### Table 2. Phase composition of the Co/Ce, Co/Ba and Co/Ce/Ba samples after the reduction estimated from Rietveld analysis (with agreement indices).

| Catalyst Symbol | Co fcc (wt%) | Co hcp | CeO₂ (%) | BaCO₃ (%) | BaCeO₃ (%) | \( \chi_\text{wp} \) (%) | \( \chi_\text{p} \) (%) | GOF |
|-----------------|-------------|--------|----------|----------|-----------|----------------|----------------|-----|
| Co/Ce           | 45          | 43ᵃ    | 12       | -        | -         | 6.29           | 4.37           | 3.25|
| Co/Ba           | 53          | -      | -        | 47       | -         | 6.57           | 3.84           | 2.92|
| Co/Ce/Ba        | 31          | 46     | -        | 15       | 8         | 6.00           | 4.63           | 1.70|

ᵃ calculated Co hcp amount in the Co/Ce catalyst is a sum of amount of pure Co hcp phase, possible stacking faults or polytypic structure.

#### 2.2. X-ray Photoelectron Spectroscopy (XPS) Studies

Evolution of the surface composition of the samples that occurred during the reduction process was investigated by XPS analysis with use of a high pressure cell. The atomic concentration of the elements present on the surface of each sample before and after the reduction was calculated. The results are shown in Table 3. Cobalt, carbon and oxygen atoms are present on the surface of all samples. Cerium and barium atoms were observed on the surface of the samples prepared with cerium and barium compounds, respectively. In the Co/Ce sample carbon signal declines after the reduction. It is most likely a result of methanation process, because carbon is considered to be a common impurity of the surface which can be present in the form of the adventitious carbon compounds. The presence of carbon on the surface of the Co/Ba and Co/Ce/Ba samples can also be assigned to the presence of barium carbonate which presence is confirmed by XRPD measurements (see Figure 1B,C). The carbon content in both mentioned above samples does not change substantially after reduction of the samples. It is in
an agreement with the presence of stable barium carbonate. A decrease of oxygen content corresponds with the reduction of cobalt oxide to metallic cobalt which is confirmed by XRPD data. A relatively high concentration of oxygen atoms in the samples after reduction corresponds with the non-reducible compounds of cerium and barium remaining in the final products of reduction. In case of the samples containing barium compounds a substantial reconstruction of the surface is induced by the reduction under hydrogen atmosphere. In both samples a substantial increase of barium compounds is observed. It indicates that not only the reduction process takes place on the surface but also a prominent mass exchange process occurs.

Table 3. Atomic concentration of Co, Ce, Ba, C and O in the samples before (unreduced) and after the reduction (reduced) estimated on the basis of the X-ray photoelectron spectra (data not presented here).

| Catalyst Symbol | Content of | Co a | Ce b | Ba c | C d | O e |
|-----------------|------------|------|------|------|-----|-----|
|                 |            | (at%)|      |      |     |     |
| Co/Ce           | unreduced  | 33   | 6    | -    | 13  | 48  |
|                 | reduced    | 69   | 16   | -    | -   | 15  |
| Co/Ba           | unreduced  | 19   | -    | 5    | 9   | 67  |
|                 | reduced    | 6    | -    | 31   | 9   | 54  |
| Co/Ce/Ba        | unreduced  | 20   | 5    | 5    | 16  | 54  |
|                 | reduced    | 6    | 1    | 21   | 29  | 43  |

a estimated on the basis of Co 3p spectra; b estimated on the basis of Ce 3d spectra; c estimated on the basis of Ba 4d spectra; d estimated on the basis of C 1s spectra; e estimated on the basis of O 1s spectra.

After the reduction the maximum of the Co 3p peak acquired for the Co/Ce/Ba sample (Figure 2) is shifted towards lower binding energy. Identical effect is also observed for other samples (data not presented). This shift proves that in all samples cobalt oxide was reduced to metallic cobalt. The observation based on XPS data is in an agreement with the results of XRPD studies (see Figure 1) and TG/DTG-MS measurements described in [11]. Both experiments indicate that the complete reduction of cobalt oxide to metallic cobalt occurs. In case of the Co/Ce and Co/Ce/Ba samples the XPS Ce 3d spectrum is altered after the reduction, indicating that the ratio of Ce$^{4+}$ to Ce$^{3+}$ ions on the surface increases. This phenomenon is thoroughly discussed for the Co/Ce sample [40]. In brief, during preparation procedure CeO$_2$ particles with disturbed surface, rich in Ce$^{3+}$ ions, are formed first. The reduction process leads to the rearrangement of the surface and formation of much more organized CeO$_2$ particles with dominant Ce$^{4+}$ ions.

![Figure 2](image-url)  
Figure 2. The high-resolution X-ray photoelectron spectra of Co 3p in the Co/Ce/Ba sample before and after the reduction.

The very distinctive effect of the reduction is the prominent increase of the barium surface content in the Co/Ba and Co/Ce/Ba samples. Its atomic concentration increases more than five times after the reduction (see Table 3). The phenomenon of surface enrichment with Ba has been previously observed.
in a barium-promoted cobalt catalyst [14]. We assume that barium compounds formed during the reduction exhibit probably lower free energy than metallic cobalt formed simultaneously and in order to minimize the surface free energy of the system they migrate to the cobalt surface and its partial coverage occurs [14,41]. According to the laws of thermodynamics, a surface creation requires work and involves a change of positive free energy. The overcoming of energy barrier of the process can be achieved by providing heat energy which is ensured during the high temperature catalysts reduction or ammonia synthesis reaction itself. In turns, in order to minimize the positive surface free energy, at which the system is the most stable, the constituent of the lowest free energy (in this case barium compounds) might migrate to the surface.

During heating of the Co/Ba and Co/Ce/Ba samples in hydrogen atmosphere, it is possible for barium oxygen compounds to form e.g. hydroxide which exhibits lower melting temperature than BaCO$_3$ and probably lower surface energy than cobalt and hence can easily wet the surface of the active phase. In that way the Ba-rich particles would screen an XPS signal coming from Co and Ce atoms, what is really observed. Unfortunately, a strong differential charging is observed especially for XPS signal of barium atoms. The signals of other elements are not influenced noticeably. It is supposed that the particles of barium-oxygen compounds are detached from the surface of the Co-Ce particles and since they are isolators a charging due to X-ray influence occurs. This effect has been observed in Ba promoted cobalt catalyst [14].

2.3. Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Figure 3 depicts SEM-EDS mapping images registered for ex-situ reduced cobalt catalysts samples promoted with barium (Figure 3A), cerium (Figure 3B) and with both additives (Figure 3C).

![Figure 3. The SEM-EDS maps of Co, Ce and Ba distribution on the surface of ex-situ reduced catalysts samples: Co/Ba (A), Co/Ce (B) and Co/Ce/Ba (C).](image-url)
Analysis of the particular maps reveals different distribution of the ingredients in the investigated samples which may hint the function of each promoter. The Co/Ba sample image (Figure 3A) indicates the non-uniform distribution of the elements on the surface. The areas rich in barium contain little or no cobalt and vice versa, areas rich in cobalt exhibit lower amount of barium. Also, the strong tendency of barium to segregate is visible which may be attributed to its ability to migrate in the reaction conditions [14]. In comparison, cobalt is distributed more uniformly across the surface. However, some areas of its increased occurrence are also present. On the surface of Co/Ce sample (Figure 3B) a more uniform distribution of elements can be observed. They are well dispersed with no significant segregation of ingredients visible. Similarly, in the Co/Ce/Ba sample (Figure 3C), all of the elements are uniformly distributed across the surface. When both promoters are present in the sample, segregation of barium, observed in Co/Ba sample, is significantly reduced, only a few small areas of increased barium presence are visible. When both promoters are present in the sample, no segregation of barium is observed, contrary to Co/Ba sample. The desired quality of the surface is attributed to the presence of cerium promoter. Barium was introduced into the systems as the last ingredient, therefore, in case of Co/Ce/Ba it was added onto more developed Co/Ce surface. On the other hand, in case of unpromoted Co sample, the specific surface area was smaller during impregnation in aqueous solution of barium nitrite. It is postulated that the cerium acts as the structural promoter [11,12] of cobalt systems which maintains good dispersion without segregation of Ba by preventing its migration via physically blocking or chemically bonding to form BaCeO$_3$ in the reaction conditions.

Additionally, the average contents of the main elements in the ex-situ reduced samples (Table 4), determined on the basis of multipoint analysis of EDS surface maps, are in a good agreement with the data presented in [11], concerning composition of the co-precipitated cobalt catalyst samples. This compliance between assumed and obtained samples composition is a good validation of applied synthesis method.

| Catalyst Symbol | Element Content (wt.%) |
|-----------------|------------------------|
|                 | Co | Ce | Ba |
| Co/Ce           | 76.8 | 9.3 | - |
| Co/Ba           | 84.1 | - | 13.7 |
| Co/Ce/Ba        | 77.3 | 9.0 | 11.3 |

2.4. Temperature-Programmed Carbon Dioxide Desorption (CO$_2$-TPD)

Basicity of the support or promoting additives plays a key role in catalysts for ammonia synthesis reaction [42–44]. Their electron-donating ability facilitates a bond dissociation in N$_2$ molecule which is considered the rate limiting step of the reaction [45]. These properties may also intensify desorption of produced ammonia molecules from the catalyst surface, thus releasing the active sites for further nitrogen adsorption [46]. Each of these effects influences the activity of the catalyst in ammonia synthesis. Therefore, using CO$_2$-TPD, surface basicity of the examined cobalt catalysts was investigated. The amount of CO$_2$ chemisorbed on the surface was determined and is given in Table 5. It can be seen that for the Co/Ce sample the amount of CO$_2$ uptake is substantial and much larger than in case of the Co/Ba and Co/Ce/Ba samples. XPS results evidently indicate that catalysts, i.e. samples after reduction, significantly differ in the composition of the surface (see Table 3). Therefore, the compounds present there may alter the interpretation of sample basicity values per unit mass or surface. To unify all values and facilitate comparison of the samples, basicity of catalysts was expressed as $\mu$mol of CO$_2$ in reference to the amount of cobalt atoms exposed on the surface after the reduction (values taken from Table 3 based on XPS results).
We are aware that such expression of basicity may be flawed, since the CO₂ molecules can adsorb not only on cobalt surface but also on a number of other sites present on the surface, although, it can be used to estimate and compare the general electron transport related properties of the working ammonia synthesis catalysts. These would include the intra-system transfer of the electrons e.g. from donors to cobalt surface and further to molecules dissociating during adsorption. The results of the calculations are given in Table 5. It can be seen that the basicity of the samples is ordered as follows: Co/Ce/Ba > Co/Ba > Co/Ce. This is in agreement with the results of the catalysts’ activity in the ammonia synthesis reaction (see Table 1). According to the data, the Co/Ce/Ba sample exhibits the highest activity and the Co/Ce sample the lowest. If we then apply the XRPD results to the picture (see Figure 1) we can conclude that the feature which distinguishes the Co/Ce/Ba catalyst from the Co/Ce and the Co/Ba is the presence of a mixed phase of barium and cerium compounds—barium cerate (BaCeO₃). This and other perovskite-type oxides (such as BaTiO₃ or BaZrO₃) have been examined previously as supports for ruthenium catalyst for ammonia synthesis in [47–50], where it was indicated that due to high basicity and high electron-donating ability, their presence greatly enhances the catalysts activity in ammonia synthesis reaction. The results for the Co/Ce/Ba sample suggest that barium cerate functions similarly in the cobalt catalysts.

The CO₂ desorption profiles are shown in Figure 4. The intensity of the signal was expressed in relation to Co atoms exposed on catalysts surface based on XPS results (see Table 3). Two signals can be observed on the desorption profiles of all catalysts – where the first one covers the range up to 150 °C and the second emerges at higher temperatures. The low-temperature signal with maximum at about 90 °C is attributed to an interaction of CO₂ molecules with weak basic sites present on the catalysts surface and relates to the Brønsted-type basic properties of the material. The CO₂ signals above 150 °C correspond to medium and strong basic surface sites. These signals can be connected with the material Lewis-type basicity and be correlated with its ability to donate electrons to the surface. The shape and location of these signals varies among the individual samples. In case of the Co/Ce and Co/Ba the second low-intensity signal extends over the entire temperature range above 150 °C. On the Co/Ce/Ba desorption profile CO₂ signal occurs much later, at about 400 °C, and extends up to 700 °C (Tmax = 560 °C). Its high intensity indicates larger number of Lewis-type basic sites on the surface what leads to increased electron-donating properties compared to other catalysts. There are no medium basic sites present on the Co/Ce/Ba surface, since no relevant mid-temperature signals were registered.

| Catalyst Symbol | CO₂ Uptake (μmolCO₂ g⁻¹) | Basicity (μmolCO₂ Surface Atom Co⁻¹) |
|-----------------|--------------------------|-------------------------------------|
| Co/Ce           | 54.4                     | 0.8                                 |
| Co/Ba           | 7.9                      | 1.3                                 |
| Co/Ce/Ba        | 8.4                      | 1.4                                 |

Table 5. The results of CO₂-TPD experiments.

![Figure 4](image-url)  
Figure 4. Carbon dioxide desorption profiles for the Co/Ce, Co/Ba and Co/Ce/Ba catalysts.


2.5. Temperature Programmed (TP) Measurements

To reveal important information about metal surfaces the temperature-programmed desorption of hydrogen (H2-TPD), nitrogen (N2-TPD) and temperature-programmed surface reaction of preadsorbed nitrogen with hydrogen (N_ads + H2 TPSR) were carried out. As a result of H2-TPD experiments hydrogen desorption profiles were obtained and presented in Figure 5. One broad peak of H2 is observed in the profile of the Co/Ce sample. The peak extends in the range of 0–400 °C with a maximum at 44 °C. Peak extent may indicate adsorption site structure inhomogeneity. In case of the Co/Ba catalyst two signals are present. The first signal has very low intensity and a maximum at 134 °C. The second, significantly more intensive one, consists of two overlapping peaks, with maxima located at 508 °C and 535 °C, respectively. In hydrogen desorption profile of the Co/Ce/Ba catalyst low-temperature and high-temperature peaks coexist. As in case of the Co/Ba sample the profile of Co/Ce/Ba is also nonhomogeneous—the low-temperature peak consists of two signals with maxima at 43 °C and 100 °C, respectively. The high-temperature peak maximum is located at 515 °C. Low and high-temperature peaks on H2 desorption profiles indicate the presence on the catalysts surface weakly and strongly hydrogen binding sites, respectively. This means that on the Co/Ce catalyst surface only weakly hydrogen binding sites occur, in case of the Co/Ba catalyst strongly binding sites dominate on the surface, while on the Co/Ce/Ba surface both types of adsorption sites coexist.

![Figure 5. Hydrogen desorption profiles for the Co/Ce, Co/Ba and Co/Ce/Ba catalysts.](image)

Nitrogen desorption profiles are depicted in Figure 6. Only one signal of nitrogen is observed on the profile of each catalyst. In case of the Co/Ce catalyst it extends in the range of low temperatures from 0 °C to about 300 °C with a maximum at 44 °C. It indicates on a weak interaction of the nitrogen molecule with the catalyst surface. In turn, on the desorption profile of the Co/Ba and the Co/Ce/Ba catalysts, the nitrogen signal appears at higher temperatures, above 400 °C, which refers to the sites binding nitrogen strongly, being present on the catalysts surface. When comparing nitrogen desorption profiles of singly promoted cobalt catalysts, i.e. the Co/Ce and the Co/Ba samples, it may be suggested that barium enhances strength of the nitrogen molecule binding to the cobalt surface—a maximum of N2 desorption peak of the Co/Ba catalyst appears at temperature of 565 °C. However, when cerium occurs alongside barium promoter (the Co/Ce/Ba catalyst) the high temperature peak shifts slightly to lower temperatures—Tonset shifts from 440 °C to 400 °C. Moreover, the peak is inhomogeneous and consists of two overlapping signals, which maxima appear at 450 °C and 535 °C, respectively.
As a result of temperature programmed surface reaction of hydrogen with preadsorbed nitrogen (N$_{\text{ads}}$ + H$_2$ TPSR), ammonia desorption profiles were registered and are presented in Figure 7. On the Co/Ce catalyst profile, the NH$_3$ signal is observed both in the range of low and high temperatures. The low temperature signal consists of three smaller peaks with maxima at 46 °C, 118 °C and 198 °C, while the high temperature signal occurs at T$_{\text{max}}$ = 655 °C. A varied shape of the desorption profile may indicate inhomogeneity of the Co/Ce sample surface. In case of the Co/Ba catalyst a signal of desorbed NH$_3$ appears only at high temperature with maximum at 653 °C. However, in case of the Co/Ce/Ba catalyst ammonia is registered both in the area of low and high temperatures. On the N$_{\text{ads}}$ + H$_2$ TPSR profile of the Co/Ce/Ba catalyst two signals of ammonia formation are detected with maxima at 270 °C and 622 °C (see Figure 7). Generally, the low temperature peaks observed on the N$_{\text{ads}}$ + H$_2$ TPSR profiles are related to adsorption sites, which bind ammonia to a surface weakly, while the high temperature ones are connected with sites binding ammonia strongly.

To sum up, H$_2$-TPD, N$_2$-TPD and N$_{\text{ads}}$ + H$_2$ TPSR experiments indicate on varied nature of the cobalt catalysts surface. Especially, as far as the Co/Ce and the Co/Ba samples are concerned—the adsorption properties of both are significantly different. Whereas, the Co/Ce/Ba sample combines the nature of both.

3. Discussion

Despite the presence of that phase was previously noted in Ce- and Ba-promoted cobalt catalysts for ammonia synthesis [11–13,39], to date no attempt has been taken to connect the observed high catalyst activity with the presence and properties of BaCeO$_3$, and consequently no detailed, dedicated and broad analysis was conducted. This study was carried out in such a manner to reflect the real reaction conditions to a highest possible degree. It allowed us to establish that the influence of...
perovskite-type barium cerate is substantial due to its specific properties. This third in situ-formed promoter combines the features of both cerium and barium additives and also introduces a new quality which results in much more active catalyst than it would be expected. Firstly, it can be explained by a high basicity, i.e. high electron-donating ability of BaCeO₃. This means that electrons can be easily transferred from the perovskite-type oxide to metal surface. There the excess of electrons located on d-orbital can be transferred to anti-bonding orbitals of N₂ molecule and facilitate its dissociation [45]. Additionally, the same increased electron density on the metal particle can prevent product poisoning by facilitating a desorption of produced ammonia from the catalyst surface, releasing active sites for nitrogen adsorption [46]. Secondly, it can be observed that in discussed materials BaCeO₃ stabilizes the hexagonal close-packed (hcp) phase of cobalt. It has been previously stated that Co hcp is more active phase of cobalt in ammonia synthesis reaction than face-centered cubic (fcc) phase [22,23]. Recently, Zhang et al. have reported that higher activity of Co hcp phase origins from the active sites’ high density of favourable shapes and adsorption energy, that are not available on Co fcc facets due to its distinct crystal structure and morphology. Authors have demonstrated that high-index facets, which are formed on hcp metal nanoparticles, facilitate a nitrogen molecule dissociation and lead to high activity of hcp phase of cobalt in ammonia synthesis [23]. The same effect was proven to occur on different hcp metals by Ahmadi and Kaghazchi [51]. Thirdly, following the literature reports of Wang suggesting that the perovskite-type oxide could be responsible for preventing hydrogen poisoning [49], we can also connect properties of the Co/Ce/Ba catalyst with this phenomenon. Although the rate limiting step in ammonia synthesis reaction is N₂ dissociation, H₂ adsorption on the metal surface is equally important. It is important not to allow for a nitrogen activation on the metal surface to be retarded by strong hydrogen adsorption, i.e. in case when significant number of active sites would be covered by H atoms. It means that the activity of the catalysts in ammonia synthesis could be low due to hydrogen covering more sites and preventing nitrogen adsorption [52–54]. Thus, a coexistence of weakly and strongly H₂ binding sites on the catalyst surface indicates that it is precluded a complete coverage of the cobalt surface with hydrogen. This beneficial property is exhibited by the Co/Ce/Ba catalyst (see Figure 5), where both weakly and strongly hydrogen binding sites co-exist on the surface. Our results stay in a good agreement with studies of Wang [49]. Fourthly, analysis of TP desorption profiles, gathered in Figures 5–7, indicate that there is a relation between the coexistence of active sites of different binding strength and ammonia synthesis occurring on the catalyst surface. One may notice that the H₂ and NH₃ desorption profiles share similarities. Therefore, the hydrogen adsorption energy and ammonia desorption from the surface (synthesis rate) must be related. It is also known that N₂ molecule does not bind strongly to the cobalt surface [23] regardless of its structure and its permanence on the surface at higher temperatures is uncertain. Therefore, to provide good performance of a catalyst, a proper balance between the particular energies must be maintained. It is important for adsorption energies of H₂ and N₂ to be close. Then, at the temperatures high enough for the N₂ activation barrier to be broken (indicated by the location of N₂ desorption peaks), the activated hydrogen atoms can persist bonded in the vicinity of dissociating N₂. When there are only low temperature H₂ adsorption sites, as in the Co/Ce sample, only small amounts of H atoms remain adsorbed on the surface in the conditions of N₂ dissociation, thus the hydrogenation is less likely to occur. Then, only little ammonia is produced, mainly from the weakly bonded hydrogen and N₂ which was activated at low temperatures. When there are only high temperature adsorption sites, as in the Co/Ba, both N and H atoms are present on the surface simultaneously at the nitrogen activation temperatures. As a result, greater amount of ammonia is produced - the desorption peak is larger. However, when the adsorption energies are similar, the active sites remain occupied and their release for new particles to be adsorbed is regulated by the ammonia formation rate and product desorption from the surface, thus the total rate is hindered. In the Co/Ce/Ba sample adsorption sites of diverse energies are present on the surface. It is beneficial in two ways. Firstly, the ammonia synthesis may occur in broader range of temperatures, as indicated by the NH₃ desorption profile. Secondly, the presence of twofold energy sites allows to accelerate the synthesis by constant accessibility of shortly occupied low energy sites which prevent
the synthesis to be inhibited by the slow product desorption blocking the high energy sites on cobalt surface. It was concluded that the presence and stabilization of both type of sites is attributed to the perovskite phase formed in situ at reaction conditions in the Co/Ce/Ba sample.

4. Materials and Methods

4.1. Catalysts Preparation

The cobalt catalysts promoted with cerium and barium, combined or separately, were the subject of basic research in our previous work, where the method of their preparation was precisely described [11]. Briefly, cobalt carbonate (Avantor Performance Materials Poland, Gliwice, Poland) and a mixture of cobalt and cerium carbonates (Acros Organics, Geel, Belgium) were prepared by precipitation and co-precipitation, respectively. Cobalt(II) nitrate hexahydrate and cerium(III) nitrate hexahydrate were used as cobalt and cerium precursors, whereas potassium carbonate was used as a precipitating agent. The precipitation was conducted in aqueous solutions of appropriate salts at 80–90 °C. The precipitates were filtered under vacuum and washed with cold distilled water several times until the pH was neutral, then dried at 120 °C overnight and calcined at 500 °C overnight in static air. In this way cobalt oxide and a mixture of cobalt and cerium oxides (designated as the Co/Ce sample) were obtained. Next, cobalt oxide and the part of the cobalt and cerium oxides mixture were impregnated by an aqueous solution of barium nitrite (Pfaltz & Bauer, Stamford, CT, USA) by using incipient wetness impregnation–multiple saturation of the sample pores with impregnating solution and drying after that. Samples were dried at 120 °C for 45 min between each of impregnation and overnight after the last impregnation. The Co/Ba and Co/Ce/Ba samples were obtained, respectively. Finally, the samples were crushed and sieved to get grains of 0.20–0.63 mm in size. In that form the Co/Ce, Co/Ba and Co/Ce/Ba materials were used in the present work. The last step of preparation was a reduction of catalysts precursors carried out directly before the measurements requiring a reduced form of the materials.

4.2. Characterization Techniques

X-ray powder diffraction (XRPD) experiments were carried out by using an XRK 900 reaction chamber (Anton Paar, Graz, Austria) mounted on an X'pert PRO diffractometer (Malvern Panalytical, Malvern, United Kingdom) working in Bragg-Brentano geometry and equipped with CuKα monochromatized radiation source (λα1 = 0.154056 nm, λα2 = 0.154439 nm). Diffraction patterns were collected with a solid-state hybrid type PIXcel1D detector (Malvern Panalytical, Malvern, United Kingdom). In the incident beam path Ni filter with 0.02 mm thickness was used, whilst in the diffracted beam path curved graphite crystal monochromator in [002] position was applied. XRPD measurements were performed in order to identify phase composition of the materials. They were analysed in two states: as-prepared (i.e. in the unreduced form) and after in situ reduction in H2-Ar mixture (20 vol% of H2; total gas flow rate 100 mL min⁻¹) at 550 °C for 5 h. Diffraction data was collected at ambient temperature and at reduction temperature (550 °C), respectively, in the scattering 2θ range of 20–100° with 0.02 step size. The PANalytical High Score Plus v.3.0e software (Malvern Panalytical, Malvern, United Kingdom) with ICDD PDF4+ database (International Centre for Diffraction Data, Newtown Square, PA, USA) was used for data analysis. The XRPD results are presented in sets of figures showing these states for a given sample. Below each figure sets of markings are introduced indicating the positions of diffraction reflections characteristic for crystallographic phases regarding each sample. A full-pattern fit based on the Rietveld refinement was used to calculate the weight fractions of the identified crystallographic phases. The accuracy of Rietveld QPA for poorly crystallized nanometric phases with contents higher than 1.0 wt. % gives relative errors lower than 20% [55].

A semi-automatic procedure of Rietveld refinement included in the HighScore Plus 3.0e software by PANalytical was used. During this procedure, the following parameters were varied: scale factor, unit cell, peak profile shape and full width at half maximum (FWHM). All initial crystal data required for Rietveld refinement was retrieved from the ICDD PDF 4+ database.
X-ray photoelectron spectroscopy (XPS) with AlKα radiation source (hv = 1486.6 eV) was used to investigate the surface composition of the samples before and after their reduction. The sample formed in a small tablet (ca. 10 mm in diameter) and placed in a sample holder was reduced in the high-pressure cell (HPC), being a part of an ultra-high vacuum (UHV) system in a flow of hydrogen (99.999 vol%, 20 mL min⁻¹) at 550 °C for 5 h. Next, the HPC was evacuated to the pressure of 1 × 10⁻⁶ mbar and the sample was transferred under UHV to the analysis chamber of an electron spectrometer. This procedure was applied to avoid the exposure of the catalyst to the air after the reduction. The pressure in the analysis chamber was kept under 1 × 10⁻⁹ mbar. XPS measurements were conducted in a Prevac (Rogów, Poland) system equipped with an SES 2002 electron energy analyser (Scienta, Omicron, Uppsala, Sweden) operating at constant transmission energy (Ep = 50 eV). The spectrometer was calibrated by using the following photoemission lines (with reference to the Fermi level): EB Ag 3d5/2 = 368.3 eV and EB Au 4f7/2 = 84.0 eV. The surface composition of the samples was calculated based on the peak area intensities of the Co 3p, Ce 3d, Ba 4d, C 1s and O 1s transitions by using the sensitivity factor approach and assuming homogeneous composition of the surface layer. Uncertainty for XPS measurements comprises peak area estimation as well as relative sensitivity and in case of the present studies is estimated below 3% of a value.

The surface morphology of the samples were observed by using a scanning electron microscope (SEM, Su-70, Hitachi, Hitachinaka, Ibaraki, Japan) equipped with a Schottky Field Emission gun of maximum acceleration voltage of 30 kV and resolution of 1 nm at 15 kV. This electron source ensures high current and brightness of the beam with ultra-high resolution which is required for analytical applications. The samples were observed using SE (secondary electron) detector. Energy Dispersive Spectrometry (EDS) was applied for the chemical analysis. Quantitative analysis as well as maps of chemical elements distribution were obtained. The value of errors of EDS analysis depends on the content of the element in the system, i.e. 2% for 100–20 wt.%, 4% for 20–5 wt.%, 20% for 5–1wt.% and up to 100% for 1–2 wt.%. The samples were mounted on aluminium stage by carbon tape.

Temperature-programmed desorption of carbon dioxide (CO₂-TPD), hydrogen (H₂-TPD), nitrogen (N₂-TPD) and temperature-programmed reaction of preadsorbed nitrogen with hydrogen (N_{ads} + H₂ TPSR) experiments were carried out in a flow set-up in a quartz U-tube reactor using fully automated AutoChem 2920 (Micromeritics Instrument Co., Norcross, GA, USA). The apparatus was equipped with a TCD cell and supplied with high purity (≥99.9999 vol%) gases. Total gas flow rate was 40 mL min⁻¹. Before all the experiments samples containing 0.3 g Co₃O₄ were reduced in a stream of H₂ at 550 °C for 17 h and after that rinsed for 1 h at 700 °C with He in case of CO₂-TPD, N₂-TPD and N_{ads} + H₂ TPSR measurements or at 570 °C with Ar in case of H₂-TPD. Next, samples were cooled in He or Ar stream to the suitable temperature in which adsorption was carried out and one of the measurements listed below was then performed:

- Temperature-programmed carbon dioxide desorption (CO₂-TPD)—adsorption of carbon dioxide was carried out at 40 °C for 2 h. Subsequently, the system was purged with He (40 °C) for 1 h. Then, temperature was raised to 700 °C with a rate of 10 °C min⁻¹ in He and the concentration of desorbing CO₂ in the outlet gas was monitored.

- Temperature-programmed hydrogen desorption (H₂-TPD)—hydrogen desorption was carried out at 150 °C for 15 min, during cooling the sample to 0 °C and at 0 °C for 15 min. Subsequently, the system was flushed with Ar (0 °C) for 1 h to remove weakly adsorbed hydrogen. Next, in Ar stream temperature was raised to 550 °C with a rate of 10 °C min⁻¹ and kept for 25 min, while monitoring the concentration of desorbing H₂ in the outlet gas.

- Temperature-programmed nitrogen desorption (N₂-TPD) and surface reaction of preadsorbed nitrogen with hydrogen (N_{ads} + H₂ TPSR)—adsorption of nitrogen was carried out at 200 °C for 14 h and during cooling the sample to 0 °C. Next, it was purged with He (0 °C) for 1 h to remove weakly adsorbed nitrogen. Then, temperature was raised to 700 °C with a rate of 10 °C min⁻¹ in He (N₂-TPD) or H₂ stream (N_{ads} + H₂ TPSR) and kept for 25 min. The concentration of desorbing molecules in the outlet gas was monitored – nitrogen or ammonia, respectively. It was assumed...
that only ammonia, as a product, was observed during N\(_{\text{ads}}\) + H\(_2\) TPSR measurements. To prove this state, an additional experiment was conducted, according to the same procedure as the main measurement, but the reactor outlet gas was cooled in a trap maintained at –86 °C. When gas was flowing through the cold trap, TCD readings indicated no products present in the stream. It was therefore concluded that the ammonia, as the only product of N\(_{\text{ads}}\) + H\(_2\) TPSR, was entirely caught in a cold trap.

5. Conclusions

In summary, the selection of suitable additives is the crucial issue for the reactivity of the cobalt catalysts for ammonia synthesis. It has been previously stated that cerium and barium compounds are essential additives in cobalt systems—cerium oxide is a structural promoter of cobalt, while barium exhibits mainly electronic character—but structural effect is also observed. However, the use of cerium and barium simultaneously is more beneficial and results in a strong synergistic catalytic effect in the cobalt system. The results of the studies indicate that the high activity of the cobalt catalyst co-promoted with cerium and barium may be related not only to the simultaneous influence of the main promoters but also to the presence of the third promoter, i.e. perovskite-type barium cerate (BaCeO\(_3\)) formed from cerium and barium precursor compounds during the catalyst activation. Despite being present only in small amounts the promoter positively affects the operation of the exposed active phase. This provides the catalyst with specific properties which are much more favourable than in case of the singly promoted system.

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References

1. Thomson, S.J. Promotion in heterogeneous catalysis: Retrospect and prospect. *J. Chem. Soc. Faraday Trans.* 1987, 83, 1893–1914. [CrossRef]
2. Kiskinova, M. Poisoning and promotion in catalysis based on surface science concepts and experiments. *Stud. Surf. Sci. Catal.* 1991, 70, 1–345. [CrossRef]
3. Hutchings, G.J. Promotion in heterogeneous catalysis: A topic requiring a new approach? *Catal. Lett.* 2001, 75, 1–12. [CrossRef]
4. Richardson, J.T. *Principles of Catalysts Development*; Springer Science+Business Media: New York, NY, USA, 1989.
5. Ryczkowski, J.; Borowiecki, T. Modyfikatory katalizatorów heterogenicznych. *Przem. Chem.* 2016, 82, 763–765.
6. Wang, X.; Li, L.; Zhang, T.; Lin, B.; Ni, J.; Au, C.T.; Jiang, L. Strong metal-support interactions of Co-based catalysts facilitated by dopamine for highly efficient ammonia synthesis: In situ XPS and XAFS spectroscopy coupled with TPD studies. *Chem. Commun.* 2019, 55, 474–477. [CrossRef]
7. Gao, W.; Wang, P.; Guo, J.; Chang, F.; He, T.; Wang, Q.; Wu, G.; Chen, P. Barium Hydride-Mediated Nitrogen Transfer and Hydrogenation for Ammonia Synthesis: A Case Study of Cobalt. *ACS Catal.* 2017, 7, 3654–3661. [CrossRef]
8. Wang, X.; Peng, X.; Chen, W.; Liu, G.; Zheng, A.; Zheng, L.; Ni, J.; Au, C.; Jiang, L. Insight into dynamic and steady-state active sites for nitrogen activation to ammonia by cobalt-based catalyst. *Nat. Commun.* 2020, 11, 1–10. [CrossRef] [PubMed]
9. Ronduda, H.; Zyburt, M.; Patkowski, W.; Tarka, A.; Jodłowski, P.; Kępiński, L.; Sarnecki, A.; Moszyński, D.; Raroğ-Pilecka, W. Tuning the catalytic performance of Co/Mg-La system for ammonia synthesis via the active phase precursor introduction method. *Appl. Catal. A Gen.* 2020, 598, 117553. [CrossRef]

10. Lin, B.; Liu, Y.; Heng, L.; Ni, J.; Lin, J.; Jiang, L. Effect of barium and potassium promoter on Co/CoO catalysts in ammonia synthesis. *J. Rare Earths* 2018, 36, 703–707. [CrossRef]

11. Raroğ-Pilecka, W.; Karolewska, M.; Truszkiewicz, E.; Iwanek, E.; Mierzwa, B. Cobalt catalyst doped with cerium and barium obtained by Co-precipitation method for ammonia synthesis process. *Catal. Lett.* 2011, 141, 678–684. [CrossRef]

12. Karolewska, M.; Truszkiewicz, E.; Mierzwa, B.; Kępiński, L.; Raroğ-Pilecka, W. Ammonia synthesis over cobalt catalysts doped with cerium and barium. Effect of the ceria loading. *Appl. Catal. A Gen.* 2012, 445–446, 280–286. [CrossRef]

13. Karolewska, M.; Truszkiewicz, E.; Wićiseł, M.; Mierzwa, B.; Kępiński, L.; Raroğ-Pilecka, W. Ammonia synthesis over a Ba and Ce-promoted carbon-supported cobalt catalyst. Effect of the cerium addition and preparation procedure. *J. Catal.* 2013, 303, 130–134. [CrossRef]

14. Zyburt, M.; Wyszyńska, M.; Tarka, A.; Patkowski, W.; Ronduda, H.; Mierzwa, B.; Kępiński, L.; Sarnecki, A.; Moszyński, D.; Raroğ-Pilecka, W. Surface enrichment phenomenon in the Ba-doped cobalt catalyst for ammonia synthesis. *Vacuum* 2019, 168, 108831. [CrossRef]

15. Hwang, S.M.; Han, S.J.; Min, J.E.; Park, H.G.; Jun, K.W.; Kim, S.K. Mechanistic insights into Cu and K promoted Fe-catalyzed production of liquid hydrocarbons via CO2 hydrogenation. *J. CO2 Util.* 2019, 34, 522–532. [CrossRef]

16. Xie, J.; Paalanen, P.P.; van Deelen, T.W.; Weckhuysen, B.M.; Louwverse, M.J.; de Jong, K.P. Promoted cobalt metal catalysts suitable for the production of lower olefins from natural gas. *Nat. Commun.* 2019, 10, 1–10. [CrossRef] [PubMed]

17. Torres Galvis, H.M.; Koeken, A.C.J.; Bitter, J.H.; Davidian, T.; Ruitenbeek, M.; Dugulan, A.I.; De Jong, K.P. Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins. *J. Catal.* 2013, 303, 22–30. [CrossRef]

18. Zafarí, R.; Abdouss, M.; Zamani, Y.; Tavasoli, A. An Efficient Catalyst for Light Olefins Production from CO Hydrogenation: Synergistic Effect of Zn and Ce Promoters on Performance of Co–Mn/SiO2 Catalyst. *Catal. Lett.* 2017, 147, 2475–2486. [CrossRef]

19. Wang, X.; Zhang, C.; Chang, Q.; Wang, L.; Lv, B.; Xu, J.; Xiang, H.; Yang, Y.; Li, Y. Enhanced Fischer-Tropsch synthesis performances of Fe/B-BN catalysts by Cu and Mn. *Catal. Today* 2020, 343, 91–100. [CrossRef]

20. Gao, J.; Mo, X.; Chien, A.C.Y.; Torres, W.; Goodwin, J.G. CO hydrogenation on lanthana and vanadia doubly promoted Rh/SiO2 catalysts. *J. Catal.* 2009, 262, 119–126. [CrossRef]

21. Jiao, Y.; Wang, J.; Qin, L.; Wang, J.; Zhu, Q.; Li, X.; Gong, M.; Chen, Y. Kerosene cracking over supported monolithic Pt catalysts: Effects of SrO and BaO promoters. *Chin. J. Catal.* 2013, 34, 1139–1147. [CrossRef]

22. Rambeau, G.; Jorti, A.; Amargliolo, H. Catalytic activity of a cobalt powder in NH₃ synthesis in relation with the allotropic transformation of the metal. *J. Catal.* 1985, 94, 155–165. [CrossRef]

23. Zhang, B.Y.; Chen, P.P.; Liu, J.X.; Su, H.Y.; Li, W.X. Influence of Cobalt Crystal Structures on Activation of Nitrogen Molecule: A First-Principles Study. *J. Phys. Chem. C* 2019, 123, 10956–10966. [CrossRef]

24. Lin, B.; Qi, Y.; Wei, K.; Lin, J. Effect of pretreatment on ceria-supported cobalt catalyst for ammonia synthesis. *RSC Adv.* 2014, 4, 38093–38102. [CrossRef]

25. Lin, B.; Liu, Y.; Heng, L.; Ni, J.; Lin, J.; Jiang, L. Effect of ceria morphology on the catalytic activity of Co/CoO catalyst for ammonia synthesis. *Catal. Commun.* 2017, 101, 15–19. [CrossRef]

26. Lee, Y.L.; Jha, A.; Jang, W.J.; Shim, J.O.; Jeon, K.W.; Na, H.S.; Kim, H.M.; Lee, D.W.; Yoo, S.Y.; Jeon, B.H.; et al. Optimization of Cobalt Loading in Co–CoO Catalyst for the High Temperature Water–Gas Shift Reaction. *Top. Catal.* 2017, 60, 721–726. [CrossRef]

27. Lee, Y.L.; Jha, A.; Jang, W.J.; Shim, J.O.; Rode, C.V.; Jeon, B.H.; Bae, J.W.; Roh, H.S. Effect of alkali and alkaline earth metal on Co/CoO catalyst for the water-gas shift reaction of waste derived synthesis gas. *Appl. Catal. A Gen.* 2018, 551, 63–70. [CrossRef]

28. Hansen, T.W.; Wagner, J.B.; Hansen, P.L.; Dahl, S.; Topsøe, H.; Jacobsen, C.J.H. Atomic-resolution in situ transmission electron microscopy of a promoter of a heterogeneous catalyst. *Science* 2001, 294, 1508–1510. [CrossRef]
29. Rossetti, I.; Pernicone, N.; Forni, L. Promoters effect in Ru/C ammonia synthesis catalyst. *Appl. Catal. A Gen.* 2001, 208, 271–278. [CrossRef]
30. Sheng Zeng, H.; Inazu, K.; Aika, K.I. The working state of the barium promoter in ammonia synthesis over an active-carbon-supported ruthenium catalyst using barium nitrate as the promoter precursor. *J. Catal.* 2002, 211, 33–41. [CrossRef]
31. Truszkiewicz, E.; Rárogy-Pilecka, W.; Schmidt-Szalowski, K.; Jodzis, S.; Wilczewska, E.; Lomot, D.; Kaszkur, Z.; Karpinski, Z.; Kowalczyk, Z. Barium-promoted Ru/carbon catalyst for ammonia synthesis: State of the system when operating. *J. Catal.* 2009, 265, 181–190. [CrossRef]
32. Zhong, Z.H.; Aika, K.I. The effect of hydrogen treatment of active carbon on Ru catalysts for ammonia synthesis. *J. Catal.* 1998, 173, 535–539. [CrossRef]
33. Bielawa, H.; Hinrichsen, O.; Birkner, A.; Mühler, M. The Ammonia-Synthesis Catalyst of the Next Generation: Barium-Promoted Oxide-Supported Ruthenium. *Angew. Chem. Int. Ed. Engl.* 2001, 40, 1061–1063. [CrossRef]
34. Freels, M.; Liaw, P.K.; Jiang, L.; Klarstrom, D.L. Advanced Structural Materials: Properties, Design Optimization, and Applications. In *Advanced Structural Materials: Properties, Design Optimization, and Applications*; Soboyejo, W.O., Srivatsan, T.S., Eds.; CRC Press: Boca Raton, FL, USA, 2007; pp. 187–224.
35. Lin, S.S.Y.; Kim, D.H.; Ha, S.Y. Metallic phases of cobalt-based catalysts in ethanol steam reforming: The effect of cerium oxide. *Appl. Catal. A Gen.* 2009, 355, 69–77. [CrossRef]
36. Ducreux, O.; Rebours, B.; Lynch, J.; Roy-Auberger, M.; Bazin, D. Microstructure of Supported Cobalt Fischer-Tropsch Catalysts. *Oil Gas Sci. Technol. Rev. IEF* 2009, 64, 49–62. [CrossRef]
37. Bulavchenko, O.A.; Cherepanova, S.V.; Tsibulya, S.V. In situ XRD investigation of Co$_3$7. [CrossRef]
38. Ahmadi, S.; Kaghazchi, P. On the origin of high activity of hcp metals for ammonia synthesis. *Phys. Chem. Chem. Phys.* 2016, 18, 5291–5298. [CrossRef]
39. Rambeau, G.; Amariglio, H. Ammonia synthesis on ruthenium powder from 100 to 500 °C and hydrogenation of preadsorbed nitrogen down to -70 °C. *J. Catal.* 1981, 72, 1–11. [CrossRef]
53. Lin, B.; Wang, R.; Lin, J.; Ni, J.; Wei, K. Sm-promoted alumina supported Ru catalysts for ammonia synthesis: Effect of the preparation method and Sm promoter. Catal. Commun. 2011, 12, 553–558. [CrossRef]

54. Wang, X.; Ni, J.; Lin, B.; Wang, R.; Lin, J.; Wei, K. Highly efficient Ru/MgO-CeO$_2$ catalyst for ammonia synthesis. Catal. Commun. 2010, 12, 251–254. [CrossRef]

55. León-Reina, L.; García-Maté, M.; Álvarez-Pinazo, G.; Santacruz, I.; Vallcorba, O.; De La Torre, A.G.; Aranda, M.A.G. Accuracy in Rietveld quantitative phase analysis: A comparative study of strictly monochromatic Mo and Cu radiations. J. Appl. Crystallogr. 2016, 49, 722–735. [CrossRef] [PubMed]