

Article

Heat Treatment-Induced Phase Evolution of Co–Mg–Fe Oxide Systems as Potential Deep Oxidation Catalysts

Alexandr Sass , Alexandr Brodskiy * , Ivan Torlopov * , Kenzhegul Rakhmetova, Atabek Khussain, Raiymbek Yersaiyn , Vladimir Yaskevich and Bolatbek Khussain

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, 142, Kunaev Str., Almaty 050010, Kazakhstan; aleksandr-sass@mail.ru (A.S.); rahmetova_75@mail.ru (K.R.); atabek.khussain@gmail.com (A.K.); yer_ray@mail.ru (R.Y.); yaskevich46@mail.ru (V.Y.); bolatbekh@mail.ru (B.K.)

* Correspondence: albrod@list.ru (A.B.); myndfrea@gmail.com (I.T.);

Tel.: +7-775-814-2053 (A.B.); +7-777-044-2077 (I.T.)

Abstract

Co–Mg–Fe oxide systems are promising candidates for thermally stable deep oxidation catalysts because they potentially combine redox-active cobalt and iron components with stabilizing magnesium-containing phases. In this work, phase formation in a Co–Mg–Fe oxide system obtained by thermal decomposition of nitrate precursors with a Co:Mg:Fe ratio of 1:1:1 was studied over a wide range of heat-treatment temperatures from 400 to 1300 °C. The samples were characterized by X-ray diffraction, Mössbauer spectroscopy, Fourier-transform infrared spectroscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy mapping, and temperature-programmed oxygen desorption. The results show that the system undergoes staged phase evolution. At 400 °C, α -Fe₂O₃, including Mg-modified hematite-like states, cobalt-containing spinel phases, and a rocksalt oxide phase, is formed. Starting from 550 °C, a mixed ferrite spinel phase appears and its content increases with temperature. The transition through 800–900 °C is accompanied by decomposition of cobalt-containing spinels, a sharp change in the inversion parameter of the mixed ferrite, and formation of a stable high-temperature combination of ferrite spinel and rocksalt oxide solid solution. Oxygen desorption is most pronounced for the low- and medium-temperature samples and decreases strongly after high-temperature treatment. The obtained results provide the basis for the design of thermally stable Co–Mg–Fe oxide catalysts for deep oxidation processes.

Keywords: cobalt oxide; magnesium oxide; iron oxide; spinel; ferrites; solid solution; combustion catalyst



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1. Introduction

Various oxide systems based on variable-valence metals, along with noble metal-based systems, play an important role in catalysts designed for gas purification from carbon monoxide and hydrocarbons, including industrial exhaust gas treatment [1–3]. Modern deep oxidation catalyst formulations require combination of high activity with resistance to overheating, water vapor, and catalyst poisons, since they operate under harsh thermal and chemical conditions [1,4]. At the same time, the practical applicability of oxide catalysts is determined not only by their activity, but also by the availability of raw materials, low production cost, and ability to retain their performance characteristics during long-term operation.

One of the more challenging tasks in catalytic deep oxidation is the combustion of residual methane. Methane is the most stable light hydrocarbon, owing to the high strength of the C–H bond; thus it requires relatively high temperatures for complete oxidation, typically in the range of 550–800 °C [5]. Under these conditions, the activity of an oxide catalyst is largely determined by the reactivity of lattice oxygen in the oxide structure, as well as by the reversibility of changes in the oxidation states of transition-metal cations [1–4].

Among transition-metal oxides, cobalt oxide Co_3O_4 and various cobalt-based spinels of the MeCo_2O_4 type exhibit high activity in the deep oxidation of hydrocarbons [6–9]. Their catalytic properties are commonly associated with the relatively low energy barrier of the $\text{Co}^{2+}/\text{Co}^{3+}$ transition in the spinel structure, the similarity of the ionic radii of cobalt cations in different oxidation states, and the ability of the spinel-type lattice to participate in lattice oxygen transfer processes [10,11]. However, supported cobalt-containing catalysts, in particular $\text{Co}/\text{Al}_2\text{O}_3$ -type systems, undergo irreversible deactivation at elevated temperatures due to the formation of the non-active CoAl_2O_4 phase [9,12]. This stimulates the search for supports, promoters, and matrix components that can stabilize the active cobalt component while limiting the formation of catalytically inert phases.

One approach to solving this problem is the use of alkaline-earth metal oxides, particularly MgO . The effect of MgO on the evolution of phase composition, oxygen reactivity in the cobalt spinel structure, and the relationship between these parameters and catalytic activity has previously been considered in detail using Co-Mg oxide systems of different compositions [13,14]. In such systems, the formation of CoAl_2O_4 during overheating can be suppressed by binding alumina into inert magnesium aluminate [15]. At the same time, magnesia and alumina are characterized by a constant valence of the corresponding cations, while oxygen in the phases formed by these oxides is only weakly involved in the redox processes that determine catalytic deep oxidation. Therefore, further development of this approach may involve replacing the inert alumina-containing component with a variable-valence metal oxide.

In this respect, iron is of a particular interest. Fe^{2+} and Fe^{3+} cations have chemical characteristics close to those of Co^{2+} and Co^{3+} cations in tetrahedral and octahedral positions of the spinel lattice [16]. This provides prerequisites for the formation of mixed ferrite and cobaltite spinels, as well as for the mutual redistribution of Co , Mg , and Fe cations between different crystallographic positions. The introduction of iron into the Co-Mg oxide system can therefore be regarded not only as a replacement of inert Al by a redox-active component, but also as a way to control phase formation, oxygen mobility, and thermal stability of the catalyst. An additional advantage of iron-containing systems is the possibility of using Mössbauer spectroscopy, which makes it possible to analyze the local environment of iron cations, their distribution between spinel sublattices, and changes in these parameters upon heat treatment.

From the viewpoint of deep oxidation catalysis, not only individual spinel phases but also multiphase oxide compositions are of interest, in which ferrite spinels, cobaltite spinels, and rocksalt oxide phases coexist [8,17]. Such systems can be considered as redox-buffer materials: $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs can jointly participate in oxygen transfer processes, whereas Mg -containing phases can perform a stabilizing function. As a result, the activity and stability of the catalyst may be governed not by a single phase, but by the nature of phase coexistence, the degree of mutual cation diffusion, and the reversibility of phase transformations with temperature variation.

The ability to control the coexistence of several phases is of particular importance in the synthesis of active and thermally stable catalysts. Introducing cobalt and magnesium in amounts exceeding those stoichiometrically required for the formation of a mixed ferrite may allow the formation of a composition in which cobalt- and magnesium-containing

oxide components are retained together with the ferrite phase. Such an approach may potentially ensure the presence of active phases over a wide temperature range while simultaneously improving the resistance of the system to high-temperature exposure.

Based on the above considerations, the general objective of this research was formulated as the development of deep oxidation catalysts based on combinations of ferrites and oxide compounds of cobalt, magnesium, and iron that retain their operability over a wide temperature range. This is especially important for high-temperature applications, since, as noted above, catalytic systems must be resistant to overheating under operating conditions.

The present paper is the first in a series of studies devoted to the formation and regeneration of catalytic systems based on Co–Mg–Fe oxide composites promising for use in deep oxidation reactions. It focuses on the formation and structural evolution of the Co–Mg–Fe oxide system obtained from nitrate precursors with a Co:Mg:Fe ratio of 1:1:1 under oxidative heat treatment conditions, i.e., during calcination in air, over a wide range of heat treatment temperatures. This stage is considered as the structural baseline for subsequent studies. Particular attention was paid to the effect of excess cobalt- and magnesium-containing components relative to the stoichiometry of the mixed ferrite on the coexistence of ferrite spinels, cobalt spinels, and a rocksalt oxide solid-solution phase, as well as on the possibility of retaining potentially active cobalt-containing phases in this system after high-temperature exposure.

2. Results

The synthesized Co–Mg–Fe catalyst samples obtained at different heat treatment temperatures were studied by X-ray diffraction, Mössbauer spectroscopy, FTIR spectroscopy, scanning electron microscopy, and temperature-programmed oxygen desorption.

2.1. X-Ray Diffraction

X-ray diffraction patterns of the Co–Mg–Fe oxide samples calcined at different temperatures are shown in Figure 1.

In the studied temperature range, reflections of several groups of crystalline phases are observed in the diffraction patterns: cobalt spinel phase (Co_3O_4 , PDF 42–1467; MgCo_2O_4 , PDF 81–671), ferrite spinel phase (MgFe_2O_4 , PDF 36–398; CoFe_2O_4 , PDF 22–1086), a rocksalt oxide phase (MgO , PDF 45–946; CoO , PDF 48–1719; or their solid solution), and, in the low-temperature region, $\alpha\text{-Fe}_2\text{O}_3$ (PDF 33–664) [9,14,18–20].

In the CMF(400) sample, reflections of the cobalt spinel phase, the rocksalt oxide phase, and $\alpha\text{-Fe}_2\text{O}_3$ are detected. Distinct reflections of ferrite spinel are weakly expressed or not observed at this temperature, indicating incomplete formation of the ferrite phase at the initial stage of heat treatment. With an increase in temperature to 550–800 °C, reflections of ferrite spinels appear and persist in the diffraction patterns, while reflections of cobalt spinels and the rocksalt oxide phase are also present.

In the low-temperature region, up to and including 800 °C, the cobalt spinel phase is one of the characteristic components of the phase composition. Starting from 900 °C, its reflections are no longer detected in the diffraction patterns, whereas reflections of ferrite spinels persist up to 1300 °C. The rocksalt oxide phase, corresponding to MgO , CoO , or their solid solution $(\text{Mg},\text{Co})\text{O}$, is observed over the entire studied temperature range. Weak reflections of $\alpha\text{-Fe}_2\text{O}_3$ are present only in the low-temperature samples and disappear upon further increase in the heat treatment temperature.

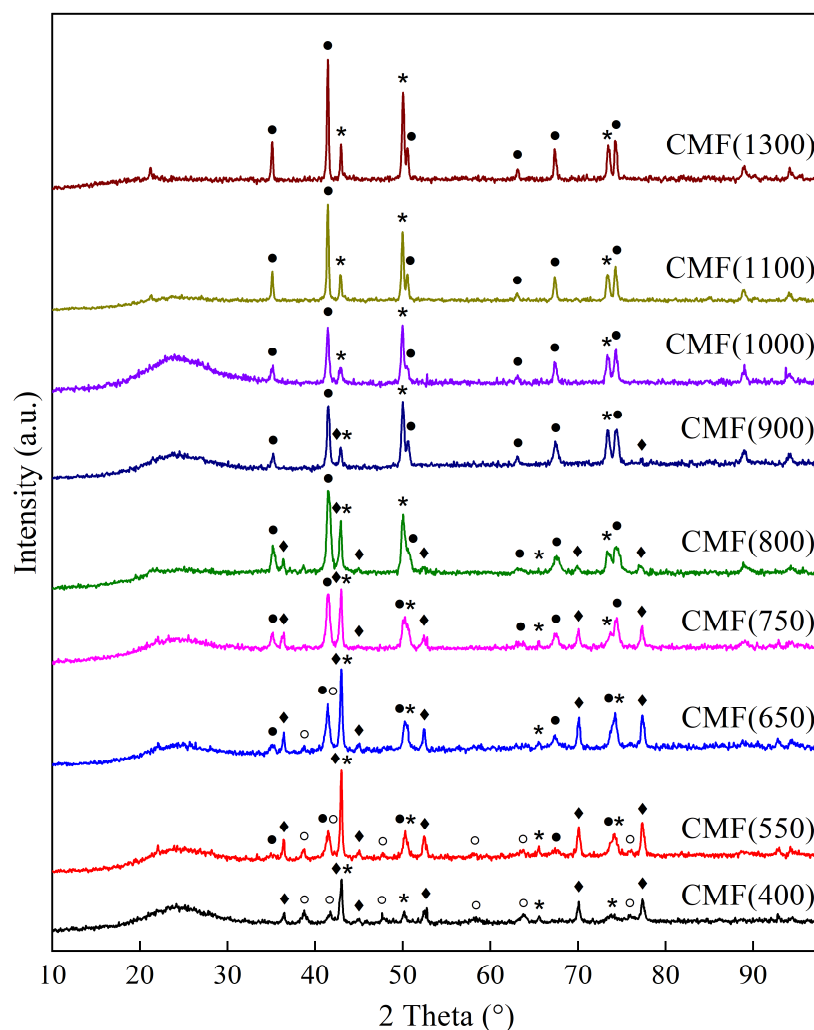


Figure 1. X-ray diffraction patterns of the samples with a Co:Mg:Fe ratio of 1:1:1 calcined at different temperatures: $\blacklozenge$ —cobalt spinel; $\bullet$ —ferrite spinel; $*$ —MgO, CoO, or a (Mg,Co)O solid solution; $\circ$ — α -Fe₂O₃.

2.2. Mössbauer Spectroscopy

Mössbauer spectra of the Co–Mg–Fe oxide samples obtained at different heat treatment temperatures are shown in Figure 2. The parameters of the spectral components are given in Table 1, and their relative contents are presented in Table 2.

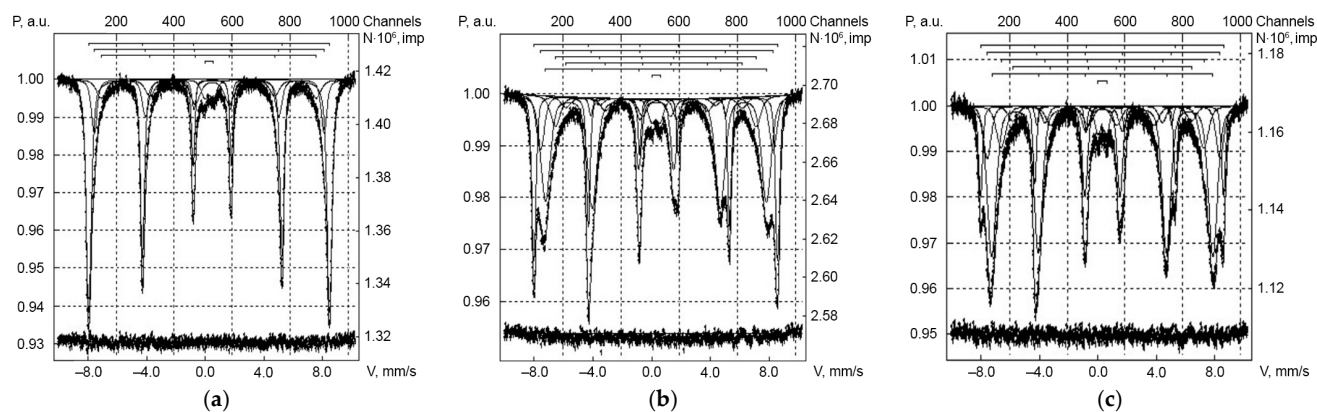


Figure 2. Cont.

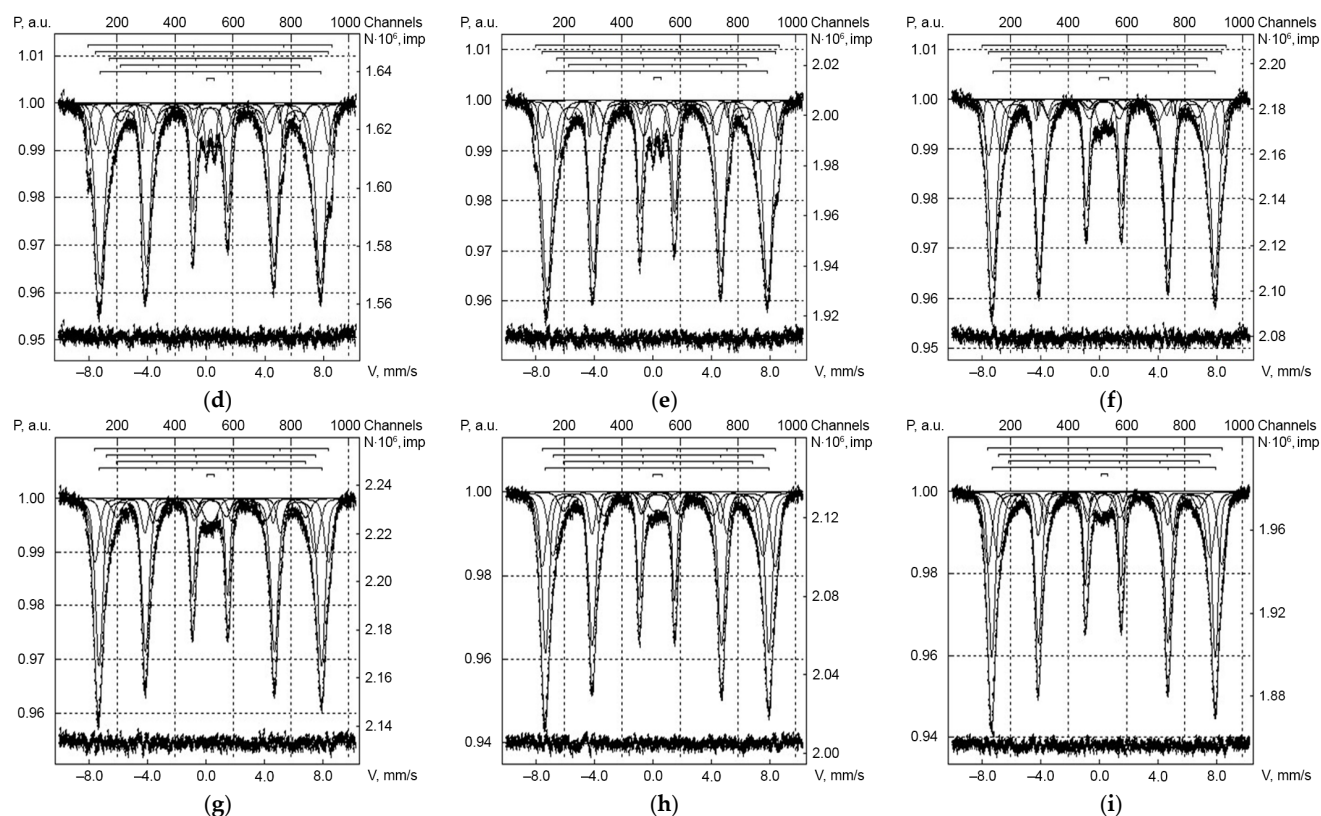


Figure 2. Mössbauer spectra of the samples with a Co:Mg:Fe ratio of 1:1:1 calcined at different temperatures: 400 (a); 550 (b); 650 (c); 750 (d); 800 (e); 900 (f); 1000 (g); 1100 (h) and 1300 °C (i). The experimental spectra are shown together with the fitted curves, the horizontal lines above the spectra indicate the positions of the resonance lines corresponding to the fitted Mössbauer spectral components, and the residuals are shown at the bottom.

Processing of the Mössbauer spectra showed that they consist of a superposition of several sextets, the number, parameters, and relative contents of which depend on the heat treatment temperature. A doublet component is also present in the spectra, with its relative content remaining almost constant.

2.3. FTIR Spectroscopy

The results of the FTIR spectroscopic study of the structure of the synthesized samples are shown in Figure 3 and summarized in Table 3.

In all samples, the main absorption bands are located in the low-frequency region of 400–700 cm^{-1} , which corresponds to vibrations of metal–oxygen bonds in oxide and spinel structures [21].

For the CMF(400) sample, bands are observed at 449, 562, and 660 cm^{-1} , together with a weak band or shoulder at approximately 525 cm^{-1} . With an increase in the heat treatment temperature to 550–800 °C, the spectra retain a three-band character. The high-frequency band near 660 cm^{-1} is preserved up to 750 °C, while for the CMF(800) sample it appears only as a shoulder near 657 cm^{-1} . After heat treatment at 900 °C and above, this band is no longer distinguished as an individual component.

The spectra of the high-temperature samples are characterized by two main bands: a low-frequency band in the region of 422–431 cm^{-1} and a band near 571 cm^{-1} . The changes in the FTIR spectra indicate a rearrangement of the oxide structure with increasing heat treatment temperature. The most pronounced change is observed during the transition from 800 to 900 °C and is manifested by the disappearance of the band near 660 cm^{-1} , consistent with the change in phase composition established by XRD and Mössbauer spectroscopy.

Table 1. Parameters of the Mössbauer spectra of the Co–Mg–Fe samples obtained at different heat treatment temperatures.

T, °C	Sextet 1			Sextet 2			Sextet 3			Sextet 4			Sextet 5			Sextet 6			Sextet 7			Doublet	
	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs	H _{eff}	Is	Qs
400	0.37	−0.21	510	0.37	−0.21	486	0.35	−0.24	455	–	–	–	–	–	–	–	–	–	–	–	–	0.26	0.60
550	0.37	−0.21	515	–	–	–	–	–	–	0.39	−0.09	492	0.33	−0.10	424	0.23	−0.02	373	0.29	−0.02	467	0.27	0.57
650	0.37	−0.21	516	–	–	–	–	–	–	0.39	−0.03	495	0.34	−0.09	430	0.28	−0.01	380	0.29	−0.01	470	0.28	0.59
750	0.37	−0.20	516	–	–	–	–	–	–	0.41	−0.00	493	0.33	−0.05	427	0.30	−0.04	380	0.29	0.00	467	0.31	0.53
800	0.38	−0.21	516	–	–	–	–	–	–	0.43	−0.03	495	0.34	−0.07	426	0.32	−0.04	377	0.29	0.00	467	0.30	0.52
900	0.39	−0.18	515	–	–	–	–	–	–	0.40	−0.05	493	0.41	−0.14	435	0.29	−0.02	395	0.29	0.00	470	0.30	0.59
1000	–	–	–	–	–	–	–	–	–	0.41	−0.05	496	0.39	−0.13	443	0.35	−0.01	401	0.27	0.02	473	0.29	0.52
1100	–	–	–	–	–	–	–	–	–	0.41	−0.06	495	0.39	−0.13	446	0.35	−0.01	401	0.27	0.02	474	0.30	0.68
1300	–	–	–	–	–	–	–	–	–	0.40	−0.07	495	0.38	−0.15	449	0.33	−0.05	403	0.26	0.03	473	0.32	0.45

Note: Is—isomer shift, mm/s; Qs—quadrupole splitting, mm/s; H_{eff}—effective magnetic field, kOe, T—heat treatment temperature, °C. A dash indicates the absence of the corresponding spectral component in the fitting model.

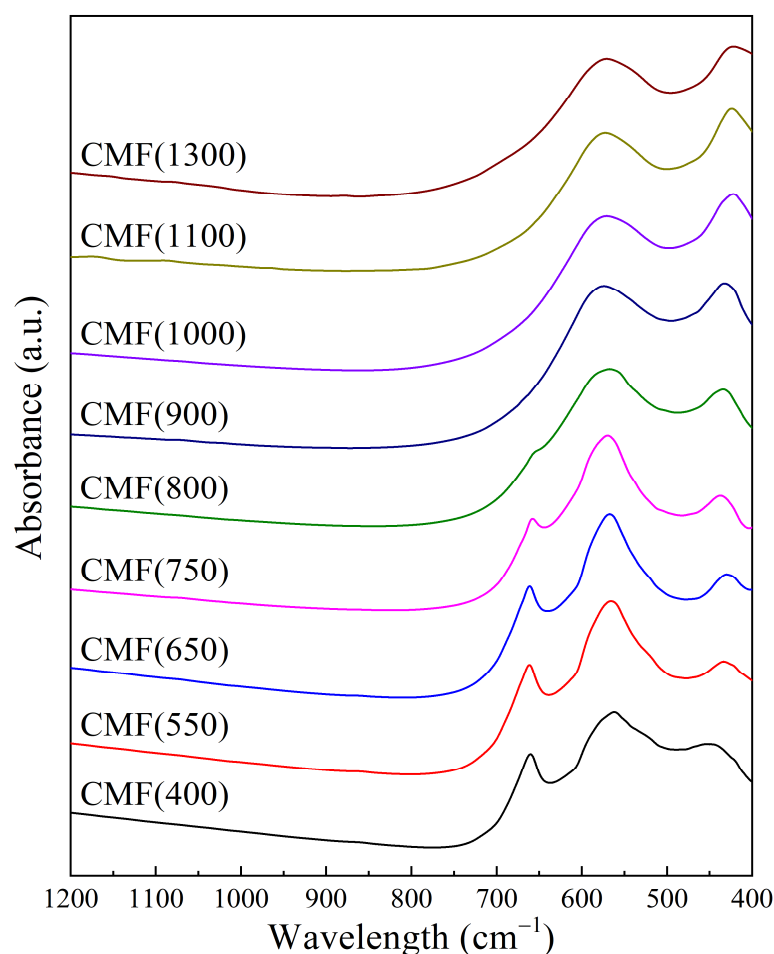
Table 2. Relative contents of the components of the Mössbauer spectra of the Co–Mg–Fe samples obtained at different heat treatment temperatures.

T, °C	Relative Content S, %							
	Sextet 1	Sextet 2	Sextet 3	Sextet 4	Sextet 5	Sextet 6	Sextet 7	Doublet
400	62	19	16	–	–	–	–	3
550	26	–	–	12	7	7	45	3
650	13	–	–	12	10	9	53	3
750	7	–	–	6	12	11	61	3
800	5	–	–	6	14	12	60	3
900	3	–	–	10	11	10	63	3
1000	–	–	–	17	13	11	56	3
1100	–	–	–	20	17	9	51	3
1300	–	–	–	20	17	12	49	2

Note: A dash indicates the absence of the corresponding spectral component in the fitting model.

Table 3. Positions of the absorption bands in the FTIR spectra of the Co–Mg–Fe samples after heat treatment at different temperatures.

Temperature, °C	Absorption Bands, cm ^{−1}
400	449, (525), 562, 660
550	435, 565, 661
650	429, 566, 661
750	436, 569, 658
800	434, 566, (657)
900	431, 572
1000	422, 571
1100	424, 572
1300	422, 571

**Figure 3.** FTIR spectra of the samples with a Co:Mg:Fe ratio of 1:1:1 calcined at different temperatures.

2.4. Scanning Electron Microscopy

The surface morphology and elemental composition of the Co–Mg–Fe samples were studied by SEM. Representative micrographs are shown in Figure 4. The complete set of elemental mapping data for the samples calcined at 400–1300 °C is presented in Figures S1–S9.

According to SEM data (Figure 4), all studied samples consist of aggregates of fine oxide particles. The samples calcined at 550–900 °C are characterized by a developed heterogeneous surface composed of agglomerated particles and voids between them. Increasing the heat treatment temperature changes the morphology: larger and denser aggregates are observed, along with signs of particle sintering. At the same time, even

after high-temperature treatment, the material retains a granular morphology and does not transform into a fully sintered monolithic structure.

Elemental mapping (Figures S1–S9) shows that Co, Mg, Fe, and O are distributed throughout the analyzed regions of the samples. The maps do not show complete separation of the system into large single-element regions, indicating the coexistence of the components within the studied scale. At the same time, the elemental distribution remains locally heterogeneous, consistent with the multi-phase nature of the Co–Mg–Fe oxide system.

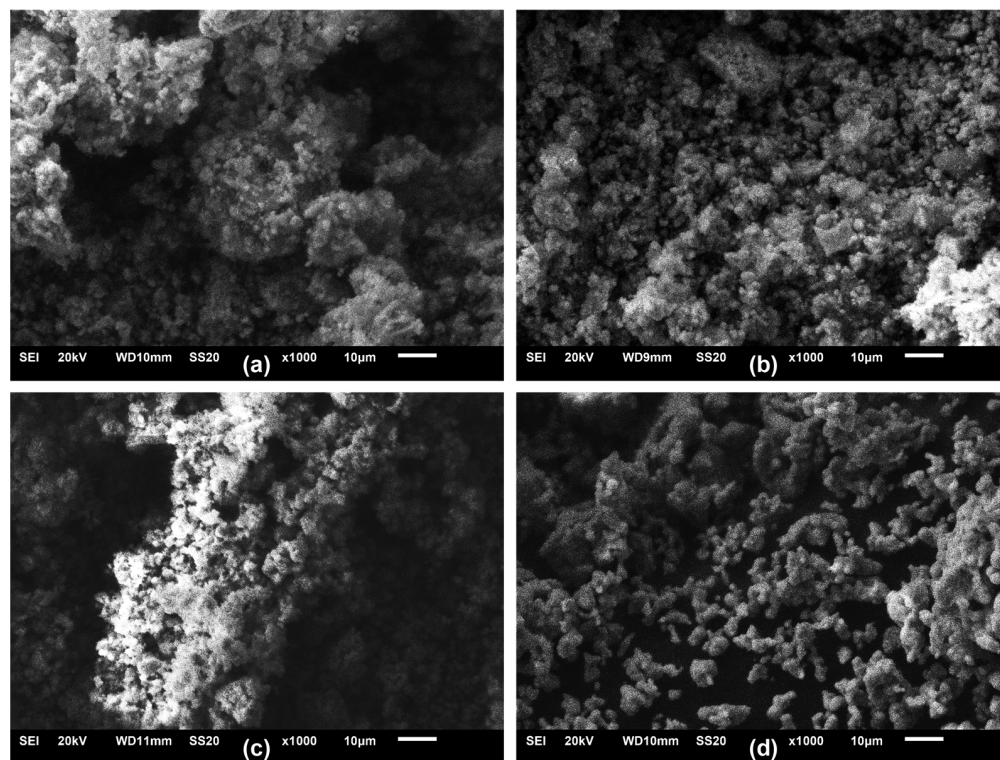


Figure 4. SEM micrographs of the Co–Mg–Fe samples after heat treatment at 550 (a), 750 (b), 900 (c), and 1300 °C (d); magnification $\times 1000$.

2.5. Temperature-Programmed Oxygen Desorption

Temperature-programmed oxygen desorption (O_2 -TPD) was used to study the reactivity of oxygen in the samples. The TPD profiles of the catalyst samples are shown in Figure 5. The quantitative characteristics of desorption are given in Table 4.

The TPD profiles of most samples are characterized by one main maximum in the high-temperature region. The exception is the CMF(400) sample, for which several oxygen desorption maxima are observed, including low- and medium-temperature regions. This indicates a more complex composition of oxygen-containing species in the low-temperature product compared with the samples calcined at higher temperatures.

For the samples treated at 550–800 °C, the main TPD maximum is located in a similar temperature region, and the signal intensity remains relatively high. With a further increase in the preliminary heat treatment temperature, a sharp decrease in the peak area is observed, especially for the samples calcined at 900 °C and above. At the same time, the general character of the profiles is retained: oxygen release occurs predominantly in the high-temperature range, but the amount of desorbed oxygen decreases significantly. The weak broad features observed for the high-temperature samples do not allow reliable determination of the maximum temperatures.

The highest amounts of released oxygen are characteristic of the samples from the low- and medium-temperature regions, whereas after heat treatment at 1000–1300 °C oxygen is released in much smaller amounts.

Table 4. TPD characteristics of the samples with a Co:Mg:Fe ratio of 1:1:1 after heat treatment at different temperatures.

Temperature, °C	Amount of O ₂ Evolved in the Temperature Range of 20–1100 °C, mmol g ^{−1}	Temperatures of O ₂ Evolution Maxima, °C
400	749.2	422, 642, 848
550	780.7	847
650	709.5	848
750	496.4	846
800	326.1	838
900	129.0	—
1000	93.9	—
1100	40.2	—
1300	6.6	—

Note: A dash indicates the absence of an oxygen evolution maximum in the corresponding TPD profile.

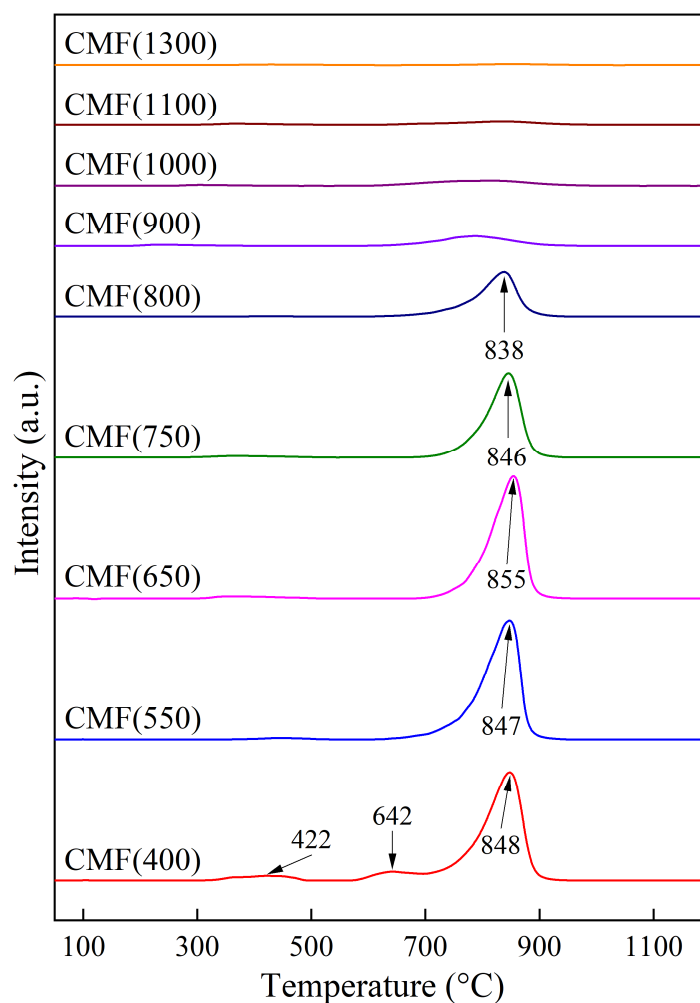


Figure 5. TPD profiles of the samples with a Co:Mg:Fe ratio of 1:1:1 calcined at different temperatures.

3. Discussion

Similar to Co–Mg oxide systems [13,14], the Co–Mg–Fe samples can be conditionally divided into two temperature regions: a low-temperature region corresponding to heat

treatment up to and including 800 °C, and a high-temperature region formed at 900 °C and above. This division is related to changes in the phase composition: during the transition to the high-temperature region, the characteristic reflections of the cobalt-containing spinel phase are no longer detected in the diffraction patterns, which is consistent with literature data on the decomposition of Co_3O_4 and cobalt spinels with the formation of CoO and CoO -based mixed oxide solid solutions [13,14,22]. In contrast to the cobalt spinel phase, the characteristic reflections of the ferrite spinel MeFe_2O_4 ($\text{Me} = \text{Mg}, \text{Co}$) persist over a wide range of heat treatment temperatures, starting from 550 °C (Figure 1) [19,23]. The rocksalt oxide phase is observed over the entire studied temperature range. Weak reflections of $\alpha\text{-Fe}_2\text{O}_3$ are also present in the diffraction patterns of the samples heat-treated up to 750 °C [20].

The lattice parameters of the different phases, calculated from the positions of the corresponding diffraction maxima, are presented in Figure 6 and Table S1.

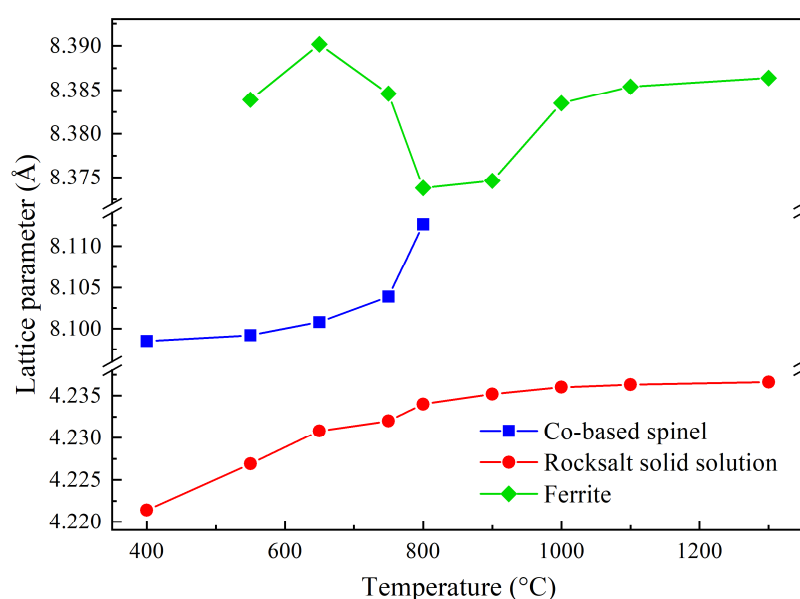


Figure 6. Average lattice parameters of the phases in the Co–Mg–Fe samples as function of heat treatment temperature.

The patterns in the variation in the lattice parameters of the different phases (Figure 6) are determined by the phase composition, redistribution of Co, Mg, and Fe between oxide and spinel structures, and, in the case of spinel phases, also by changes in the degree of inversion of their lattices [24].

For the cobalt spinel phase, a monotonic increase in the lattice parameter is observed up to the region of its decomposition at 800–900 °C, from a value close to that of cobalt and cobalt–magnesium systems ($\sim 8.09\text{--}8.10$ Å) [13,14,18,25] to 8.113 Å at a temperature close to the decomposition region. This may be associated with an overall disordering of the cation distribution due to enhanced diffusion processes with increasing heat treatment temperature.

The ferrite phase exhibits a more complex dependence of the lattice parameter on the heat treatment temperature (Figure 6). In the range of 550–650 °C, the lattice parameter is 8.385–8.390 Å; then, at 750–900 °C, it decreases to ~ 8.375 Å, after which it increases again at higher temperatures. The minimum lattice parameter of the ferrite phase coincides with the region of the most intense changes in the cobalt-containing spinel phase, indicating the interrelation of the phase transformations. This behavior can be considered as a result of mutual cation diffusion between the cobalt and ferrite spinel phases, as well as changes in the cation distribution within the ferrite structure.

For the rocksalt oxide phase, the lattice parameter increases monotonically with increasing heat treatment temperature. In the low-temperature samples, its value is close to the lattice parameter of MgO (4.211 Å [13]), whereas the subsequent increase may be associated with gradual enrichment of this phase with cobalt [14]. At the same time, the slowing down of the lattice-parameter increase in the high-temperature region indicates that the composition of the rocksalt oxide phase approaches a more stable state.

The average particle sizes of the phases in the samples, determined from XRD data, are presented in Figure 7 and Table S2.

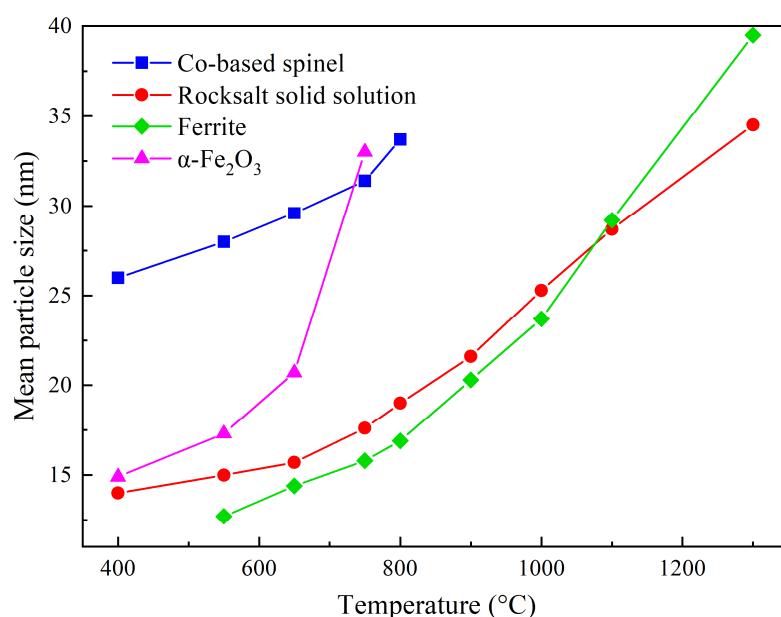


Figure 7. Average particle sizes of the phases in the Co–Mg–Fe samples as function of heat treatment temperature.

For all detected phases, an increase in the average particle size is observed with increasing heat treatment temperature (Figure 7), corresponding to crystallite growth and the development of sintering processes. At the same time, the absence of pronounced extrema in the temperature dependences of the particle sizes may indicate the absence of noticeable amorphization of the phases during heat treatment; the main phase transformations are primarily accompanied by changes in phase composition and cation distribution.

The Mössbauer spectroscopy data (Figure 2, Tables 1 and 2) are consistent with the XRD results and provide additional information on changes in the local environment of iron cations.

At 400 °C, the Mössbauer spectrum represents a superposition of three sextets and a weak doublet component. The main contribution to the spectrum is made by sextet 1. Sextets 1–3 have I_s and Q_s values close to those characteristic of hematite α -Fe₂O₃. At the same time, whereas the H_{eff} value for sextet 1 differs only slightly from the tabulated value [26], the effective magnetic fields for the other two sextets differ, indicating the presence of several non-equivalent local environments of iron ions [27]. In addition, the H_{eff} values for sextets 2 and 3 are significantly lower (Table 1), which may indicate the presence in the local environment of iron of a metal cation with a lower atomic number and fewer, or no, 3d-electrons compared with Fe. Such substitution disturbs the Fe³⁺–O–Fe³⁺ superexchange interaction and leads to a decrease in the effective magnetic field [28,29], this effect being most pronounced for sextet 3 (Table 1). Thus, according to the Mössbauer spectroscopy data, the Co–Mg–Fe system at 400 °C contains hematite α -Fe₂O₃, including hematite-like states with modified parameters, namely lower H_{eff} values.

In the hematite crystal lattice, Fe^{3+} cations occupy octahedral positions in the close-packed oxygen framework, forming layers alternating with oxygen layers, whereas the tetrahedral positions remain unoccupied. During the interaction of hematite with MgO , magnesium cations can occupy octahedral positions, replacing Fe^{3+} ions and changing their local environment. Such substitution should be accompanied by some lattice expansion, since the ionic radius of Mg^{2+} is larger than that of Fe^{3+} , as well as by the formation of oxygen vacancies to maintain electroneutrality. As a result, the formation of an Mg-modified hematite-like phase $\alpha\text{-Fe}_{2-x}\text{Mg}_x\text{O}_{3-\delta}$ is expected, with disturbed $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ superexchange interaction [30,31]. Accordingly, sextets 2 and 3 with lower H_{eff} values correspond to Fe states whose local environment contains different amounts of Mg cations [32,33]. At the same time, based on the H_{eff} values for sextets 1–3, it can be assumed that cobalt oxide Co_3O_4 is practically not involved in the modification of the hematite-like phase [34,35].

Increasing the heat treatment temperature to 550 °C leads to the disappearance of sextets 2 and 3 from the spectrum and, simultaneously, to the appearance of four new sextets (4–7) with significantly lower Q_s values, as well as different I_s and H_{eff} values (Table 1). In addition, a noticeable decrease in the relative content of $\alpha\text{-Fe}_2\text{O}_3$ occurs, whereas the relative content of the doublet component remains almost unchanged.

With a further increase in the heat treatment temperature, the relative content of hematite $\alpha\text{-Fe}_2\text{O}_3$ continues to decrease until its complete disappearance at temperatures above 900 °C. The doublet component, corresponding to a finely dispersed oxide fraction, remains almost unchanged. The processes that led to the appearance of sextets 4–7 continue to develop with increasing heat treatment temperature, as indicated by the temperature dependences of their Mössbauer parameters (Table 1) and relative contents (Table 2).

The transformations occurring in the Co–Mg–Fe system with changing heat treatment temperature, as applied to sextets 4–7, can be described within the framework of ferrite phase formation. Ferrite phases in systems of this composition have a spinel structure and include tetrahedral A positions and octahedral B positions in the oxygen framework, which are available for metal cations. The appearance of sextets 4–7 corresponds to the formation of several non-equivalent iron states in the ferrite spinel phase; in this case, the phase may be considered a mixed ferrite $(\text{Co,Mg})\text{Fe}_2\text{O}_4$ [36].

It can be assumed that sextets 4–7 correspond to iron states located in different spinel sublattices, namely tetrahedral A positions and octahedral B positions. According to Mössbauer spectroscopy data for Co–Mg ferrites, the effective magnetic field at Fe in the B sublattice is generally higher than that in the A sublattice [37–39]. Therefore, based on the effective magnetic field values, sextets 5 and 6 can be assigned to Fe cations with different local environments located in A positions, whereas sextets 4 and 7 can be assigned to Fe cations with different local environments located in B positions. Sextets 6 and 7 most likely correspond to states in which the local environment of Fe contains more Mg cations compared with sextets 4 and 5.

The data in Tables 1 and 2 allow us to examine in detail the changes in the parameters of Fe cations located in different crystallographic positions as a function of heat treatment temperature. The isomer shifts in the B sublattice (sextets 4 and 7) and the effective magnetic field H_{eff} for sextet 7 are weakly sensitive to the heat treatment temperature. At the same time, the temperature dependence of the quadrupole splitting for sextets 4 and 7 has a weakly pronounced extremal character, reaching a minimum in the region of 750 °C.

For the A sublattice, the isomer shift in sextet 5 is practically independent of temperature; the same behavior is observed for the quadrupole splitting of sextet 6. The temperature dependence of the quadrupole splitting for sextet 5, as in the case of sextets 4 and 7 of the B sublattice, has an extremal character. The isomer shift in sextet 6 increases

with increasing temperature, similarly to the behavior observed for the effective magnetic fields of sextets 5 and 6.

The changes in the Mössbauer parameters of the sextets can be explained by redistribution of metal cations between the A and B sublattices of the spinel, as evidenced by the temperature dependence of the inversion parameter λ (Figure 8), calculated using the following equation:

$$\lambda = \frac{2S_A}{S_A + S_B}, \quad (1)$$

where S_A and S_B are the areas corresponding to A and B positions occupied by Fe^{3+} cations; S_A is the sum of the areas of sextets 5 and 6; and S_B is the sum of the areas of sextets 4 and 7.

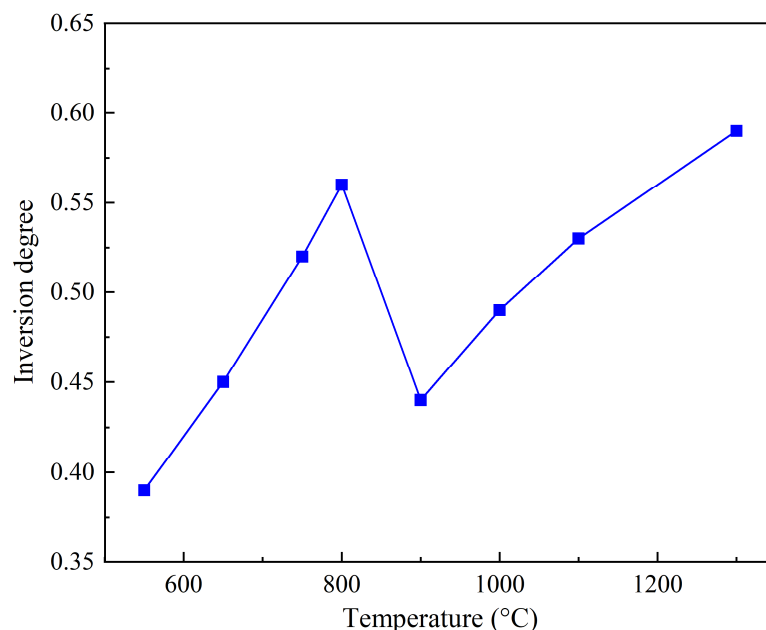
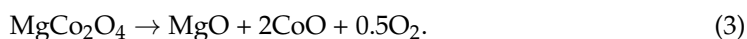


Figure 8. Temperature dependence of the inversion parameter of the mixed ferrite $(\text{Co,Mg})\text{Fe}_2\text{O}_4$ according to Mössbauer spectroscopy data.

With increasing heat treatment temperature up to 800 °C, the inversion parameter λ increases (Figure 8), indicating redistribution of Fe^{3+} cations between the B and A sublattices through their displacement from the B sublattice to the A sublattice. Both Mg^{2+} and Co^{2+} cations may participate in this process. Changes in the local environment of iron in the B sublattice are indicated by variations in the quadrupole splitting values for sextets 4 and 7 (Table 1). At the same time, since the H_{eff} values remain approximately constant, it can be assumed that the effects of cobalt and magnesium cations on the hyperfine magnetic field are mutually compensated: the incorporation of Mg^{2+} cations into the local environment of Fe^{3+} should decrease H_{eff} [32,33], whereas the presence of Co^{2+} cations may contribute to its increase [38,39].

The redistribution of Fe^{3+} between the B and A sublattices as a result of changes in the occupancy of these positions by Mg^{2+} and Co^{2+} cations leads to changes in the Mössbauer parameters of sextets 5 and 6 (Table 1). It is particularly important to note the increase in H_{eff} for both sextets, which can be associated with an increase in the fraction of Fe^{3+} cations in A positions.

The significant decrease in the inversion parameter λ in the range of 800–900 °C coincides with the temperature region of Co_3O_4 and MgCo_2O_4 decomposition [13,14]. In an oxidative atmosphere, the decomposition of these phases can be described by the following schemes:



Since the initial amounts of cobalt and magnesium nitrates exceeded the stoichiometric amounts required for the formation of the mixed ferrite $(\text{Mg,Co})\text{Fe}_2\text{O}_4$, the decomposition of Co_3O_4 and the Mg–Co spinel phase results in the formation of an additional amount of CoO- and MgO-containing oxide components in the system. Under these conditions, Co^{2+} and Mg^{2+} cations may participate in the redistribution of cations between the A and B sublattices of the ferrite spinel, leading to a decrease in the inversion parameter λ (Figure 8).

At heat treatment temperatures above 900 °C, the inversion parameter λ begins to increase again. This indicates continued redistribution of Fe^{3+} cations between the B and A sublattices through their displacement from the B sublattice to the A sublattice. The observed extrema and the character of the changes in the Mössbauer parameters of the sextets are in good agreement with the temperature region of Co_3O_4 and $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ decomposition, which makes it possible to relate these changes to the formation of additional CoO- and MgO-containing components.

Summarizing the data obtained by Mössbauer spectroscopy, it can be concluded that the transformations of iron-containing components in the Co–Mg–Fe system proceed in stages and are determined by the heat treatment temperature. At 400 °C, iron is predominantly present as $\alpha\text{-Fe}_2\text{O}_3$ and hematite-like states ($\alpha\text{-Fe}_{2-x}\text{Mg}_x\text{O}_{3-\delta}$), which differ in their local environment and lower effective magnetic field values. These states may be associated with partial modification of hematite by magnesium cations and disturbance of the $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ superexchange interaction. The weak doublet component indicates the presence of a small amount of a finely dispersed oxide fraction, whose contribution remains practically unchanged upon further increase in temperature [40].

With increasing heat treatment temperature, the formation of the ferrite phase, namely the mixed ferrite $(\text{Co,Mg})\text{Fe}_2\text{O}_4$, begins. This process is characterized by changes in the occupancy of the A and B sublattices by Mg^{2+} , Co^{2+} , and Fe^{3+} cations. The process depends on temperature and on factors associated with the initial excess of magnesium and cobalt nitrates. The most pronounced rearrangement of the cation distribution is observed in the range of 800–900 °C, after which the ferrite phase content reaches its maximum values with a further increase in temperature.

Comparison of the Mössbauer spectroscopy data with the XRD results (Figure 9) allows us to relate these local changes in the iron environment to the general sequence of phase transformations in the system.

At 400 °C, XRD detects $\alpha\text{-Fe}_2\text{O}_3$, a rocksalt oxide phase whose lattice parameter corresponds to MgO, and a cobalt-containing spinel phase. This is consistent with the Mössbauer spectroscopy data indicating the presence of hematite-like iron states and the absence of a pronounced ferrite component. The quantitative estimation of the phase composition (Figure 9) shows that, at this temperature, the $\alpha\text{-Fe}_2\text{O}_3$ content is approximately 60%, whereas the contribution of the cobalt-containing spinel phase is about 30% and that of the MgO-type rocksalt phase is about 10%. However, it should be noted that these values characterize the ratio of crystallized phases rather than the elemental composition of the sample; therefore, a significant fraction of Co and Mg is presumably retained in an X-ray amorphous or poorly crystallized state and has not yet formed crystallized oxide structures.

Upon transition to 550 °C, Mössbauer spectroscopy indicates the formation of the ferrite spinel phase, as evidenced by the presence of sextets 4–7 in the spectrum (Figure 2, Tables 1 and 2). This phase also appears in the diffraction patterns, while the content of the cobalt-containing spinel phase reaches a maximum value close to 45% (Figure 9).

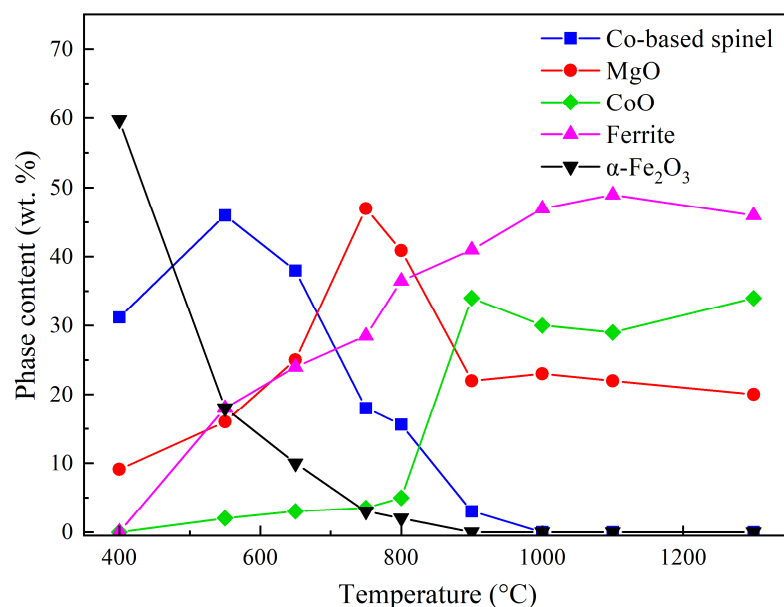


Figure 9. Effect of heat treatment temperature on the relative content of crystalline phases in the Co–Mg–Fe oxide system.

In the range of 650–750 °C, simultaneous development of the ferrite phase, preservation of cobalt-containing spinel phases, and changes in the parameters of the rocksalt oxide phase continue to be observed. In this temperature range, the fraction of α -Fe₂O₃ consistently decreases, the ferrite phase content increases, and the MgO content passes through a maximum at 750 °C (Figures 1 and 9, Tables 1 and 2).

The range of 750–900 °C is transitional: according to XRD, the characteristic reflections of cobalt-containing spinels disappear in this region, whereas Mössbauer spectroscopy shows a sharp decrease in the inversion parameter of the mixed ferrite phase. This indicates a rearrangement of the local environment of iron, which can be associated with the decomposition of cobalt-containing spinel phases and the formation of additional CoO- and MgO-containing components (Figure 9). Cation redistribution promotes the establishment of a new, more ordered structural state (Figure 8).

At temperatures of 900 °C and above, the ferrite spinel phase is retained as the only crystalline iron-containing phase (Figures 2 and 9, Tables 1 and 2). At the same time, the inversion parameter λ begins to increase again (Figure 8), indicating further changes in the occupancy of the A and B sublattices by metal cations in the already formed high-temperature system.

In the range of 1000–1300 °C, the ferrite phase content determined by XRD is approximately 45–50% (Figure 9). The amounts of CoO- and MgO-containing components change only slightly with increasing temperature above 900 °C and are approximately 30–35% and 20–23%, respectively.

Further studies were carried out using FTIR spectroscopy, since this method is particularly sensitive to changes in metal–oxygen bonds in oxide and spinel structures. In the FTIR spectra of the samples (Figure 3, Table 3), the main absorption bands are located in the region of 400–700 cm^{−1}, corresponding to Me–O vibrations in oxides and spinels [14,21,22,41]. For the low-temperature samples CMF(400)–CMF(800), the spectra have a three-band character, with bands observed in the regions of 430–450, 560–570, and 655–660 cm^{−1}; for CMF(400), an additional weak shoulder near 525 cm^{−1} is detected. The most noticeable change is the gradual weakening of the high-frequency band near 660 cm^{−1}: it is retained for the samples calcined at 400–750 °C, appears only as a shoulder at ~657 cm^{−1} in CMF(800), and is no longer distinguished as an individual component after heat treatment

at 900 °C and above. Taking into account that the band at 660 cm^{-1} corresponds to the ν_2 Me–O stretching vibrations of the cobaltite spinel phase (Co_3O_4 , MgCo_2O_4) [21,22,42] and is not characteristic of the other phases formed in the Co–Mg–Fe oxide system [43,44], this behavior is consistent with the decomposition of the cobalt-containing spinel phase during the transition to the high-temperature region. For the CMF(900)–CMF(1300) samples, the FTIR spectra are characterized by two bands in the regions of 422–431 and $571\text{--}572\text{ cm}^{-1}$. These bands presumably reflect the combined contribution of the ferrite spinel phase and rocksalt oxide components; therefore, they should not be unambiguously assigned to a single individual phase.

The band positions at $565\text{--}572$ and $425\text{--}435\text{ cm}^{-1}$ may simultaneously belong to several phases: hematite $\alpha\text{-Fe}_2\text{O}_3$, ferrites MgFe_2O_4 and CoFe_2O_4 [43,44], and the (Mg,Co)O solid solution [14,42]. According to the literature, the ν_1 band position of CoFe_2O_4 is higher than that of MgFe_2O_4 ($575\text{--}595$ vs. $565\text{--}580\text{ cm}^{-1}$) [43], whereas the ν_2 band position of the ferrite phase remains relatively constant. In contrast, for the (Mg,Co)O phase, an increase in cobalt content is accompanied by a shift in the band position to the longer-wavelength region [14]. Accordingly, the FTIR spectroscopy data confirm that, at low temperatures, the ferrite phase is enriched to a greater extent with Mg than with Co, whereas decomposition of the cobaltite spinel in the Co–Mg–Fe samples at elevated temperatures leads to enrichment of the solid-solution and ferrite phases with Co. This is in good agreement with the data obtained by the other analytical methods.

The FTIR spectroscopy data, as well as the XRD and Mössbauer spectroscopy results, characterize the phase and structural state of the oxide and spinel components. Additional information on how these components are distributed in the material at the microscale is provided by SEM and EDS mapping.

According to SEM, increasing the heat treatment temperature is accompanied by the coarsening of aggregates and the development of sintering features, which is consistent with the increase in the average particle sizes determined from XRD data. At the same time, even after high-temperature treatment, the material retains a granular morphology. This indicates that the phase transformations occur in a system of closely contacting oxide particles and aggregates (Figure 4). To quantitatively evaluate the spatial correlation of the elemental distributions, Pearson correlation coefficients R were calculated between the intensities of the Co, Mg, and Fe signals on the EDS maps (Figure 10).

In the low-temperature CMF(400) sample, the correlation between Co and Fe is higher than the correlations involving Mg. This may indicate that Co- and Fe-containing oxide components begin to crystallize earlier, whereas the Mg-containing part of the material is retained to a greater extent as a highly dispersed, poorly crystallized phase or as a component distributed within the oxide matrix (Figure 9). This behavior is consistent with the concept of crystalline phase formation from a common Co–Mg–Fe–O precursor, in which the crystallization of individual components occurs at different heat treatment temperatures. In this case, at the initial stage, the limiting processes may be the nucleation and growth of the Mg-containing rocksalt oxide phase, whereas at higher temperatures the limiting process may shift toward the diffusion of Mg^{2+} , Co^{2+} , and Fe^{3+} between the already formed oxide and spinel regions.

Upon transition to $550\text{--}650\text{ °C}$, the correlation coefficients for these element pairs increase sharply and then remain high. Thus, EDS mapping suggests that the oxide phases form in close contact and do not separate into large regions enriched with only one of the elements.

It was important to establish how these structural changes are related to oxygen mobility. For this purpose, temperature-programmed oxygen desorption profiles were obtained and analyzed (Figure 5, Table 4).

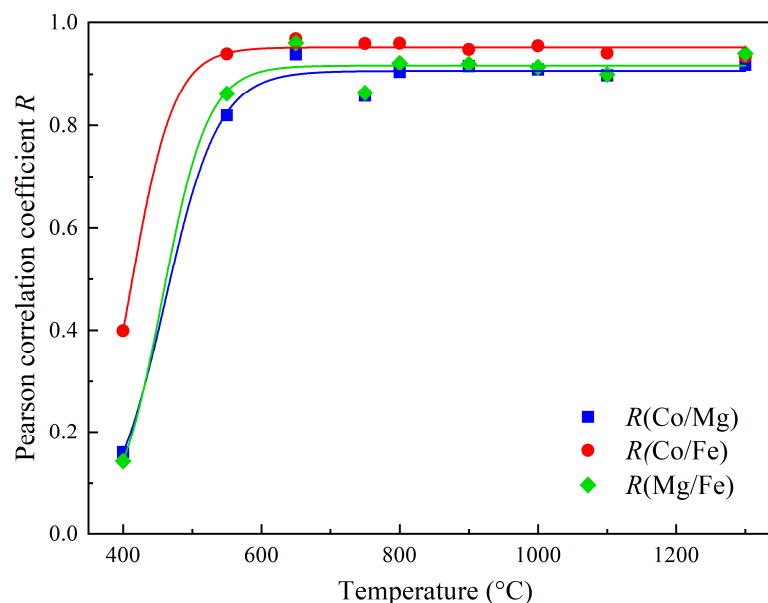


Figure 10. Pearson correlation coefficients R for the Co/Mg, Co/Fe, and Mg/Fe pairs as functions of heat treatment temperature. Symbols represent calculated Pearson correlation coefficients obtained from EDS elemental maps; lines represent smoothed trend curves.

The TPD profile of the CMF(400) sample has the most complex character and includes several oxygen evolution regions. The low-temperature maximum can be associated with the removal of the most mobile surface or weakly bound oxygen species. The medium-temperature region likely reflects oxygen release from defective iron-containing oxide states, including the Mg-modified hematite-like phase, whereas the high-temperature maximum is associated with more strongly bound lattice oxygen of cobalt-containing spinel phases.

For the samples calcined at 550–800 °C, the TPD profiles become simpler and are characterized by one main high-temperature maximum. In this case, oxygen evolution is associated with high-temperature decomposition of cobalt spinels. With increasing preliminary heat treatment temperature, the amount of lattice oxygen decreases, indicating the gradual depletion of the most reactive oxygen species and the transition of the system to a more stable state.

The sharpest decrease in the amount of evolved oxygen is observed upon transition to the samples calcined at 900 °C and above. This temperature region coincides with the disappearance of the cobalt spinel phase according to XRD (Figure 9) and with the sharp change in the inversion parameter of the mixed ferrite according to Mössbauer spectroscopy (Figure 8). Therefore, the decrease in the oxygen capacity of the system can be related to the decomposition of cobalt-containing spinel components and the formation of a more stable high-temperature combination of redox-active ferrite spinel and the rocksalt solid solution (Co,Mg)O. In such a system, the fraction of oxygen species capable of thermodesorption becomes substantially lower, which is consistent with the almost complete disappearance of distinct peaks in the TPD profiles of the samples subjected to high-temperature treatment (Figure 5, Table 4).

The obtained structural and O₂-TPD data allow the possible catalytic relevance of the observed phase evolution to be discussed. In the low- and medium-temperature samples, cobalt-containing spinel phases coexist with iron-containing oxide states and the developing ferrite spinel phase. These phases may provide structural prerequisites for oxidation catalysis because cobalt-containing spinels can participate in redox processes involving Co²⁺/Co³⁺ cations and lattice oxygen [13,14]. The relatively high oxygen release observed by O₂-TPD for the samples calcined at 400–800 °C indicates the presence of

oxygen species capable of thermodesorption, which is relevant for oxidation processes at low and medium temperatures.

The transition through the 800–900 °C region leads to decomposition of cobalt-containing spinels, formation of additional CoO- and MgO-containing rocksalt oxide components, and rearrangement of the cation distribution in the mixed ferrite spinel, accompanied by a sharp decrease in oxygen capacity. At the same time, the high-temperature samples retain a combination of ferrite spinel and rocksalt solid solution. Such a phase combination may be relevant for thermally stable oxidation catalysts, since the ferrite spinel can possibly provide a redox-active framework involving iron and cobalt cations, whereas Mg-containing oxide components may contribute to structural stabilization under high-temperature conditions [13].

Compared with binary Co–Mg oxide systems [13,14], the ternary Co–Mg–Fe composition additionally forms a ferrite spinel phase that remains stable over a wide heat treatment temperature range. The presence of Mg-containing rocksalt oxide components may contribute to stabilization of the oxide matrix and affect cation redistribution between the spinel and oxide phases, while the presence of cobalt-containing spinels and oxide components introduces additional active cobalt centers and oxygen capacity.

Therefore, the present results identify structural features that control catalytic activity: the presence and decomposition of cobalt-containing spinels, the formation and inversion of the mixed ferrite phase, the coexistence of ferrite and rocksalt oxide phases, and the temperature-dependent oxygen capacity. Thus, this combination of phases can be considered a basis for the further use and study of this system as a thermally stable oxidation catalyst.

4. Materials and Methods

4.1. Catalyst Preparation

Cobalt-magnesium-iron oxide catalysts were synthesized by thermal decomposition of nitrate precursors [13,14]. Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Sigma–Aldrich, Burlington, MA, USA), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$, Sigma–Aldrich, Burlington, MA, USA), and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99\%$, Sigma–Aldrich, Burlington, MA, USA) were used as starting reagents. The salts were taken in a molar ratio of Co:Mg:Fe = 1:1:1 and dissolved in distilled water under stirring. The resulting solution was evaporated on a magnetic stirrer under continuous stirring with a gradual increase in temperature from 100 to 180 °C over 8 h. The use of a common nitrate solution ensured mixing of Co, Mg, and Fe cations at the precursor stage, promoting the formation of a highly dispersed and homogeneous product after nitrate decomposition. The resulting dry residue was transferred to a muffle furnace and subjected to preliminary heat treatment at 275 °C for 15 h. The product was then thoroughly ground and calcined at different temperatures.

The main heat treatment was carried out in air in a muffle furnace at 400, 550, 650, 750, 800, 900, 1000, 1100, and 1300 °C. The heating rate was 10 °C min^{−1}, the holding time at the target temperature was 1 h. After calcination, the samples were quickly removed from the furnace and cooled to room temperature in air. The obtained samples were denoted as CMF(T), where CMF corresponds to the Co–Mg–Fe oxide system and T is the heat treatment temperature, °C.

4.2. Catalyst Characterization

The phase composition and structural parameters of the samples were studied by X-ray diffraction (XRD). Diffraction patterns were recorded on a DRON-4-07 powder diffractometer (Burevestnik, Saint Petersburg, Russia) using Co K α radiation and a Ni filter. The measurements were performed in the 2 θ range of 10–90° with a step size of 0.02°. Phase

identification was carried out according to the positions of the diffraction maxima using the Powder Diffraction File (PDF) database. The relative contents of the phases were estimated semi-quantitatively from the positions and areas of the corresponding diffraction maxima using PDXL 2 software, v. 2.8.4.0. When constructing the dependences of the relative phase contents, the contributions of MgO and CoO within the rocksalt solid solution were considered as a semi-quantitative estimate of the composition of the solid solution phase, taking into account the position, shape, and area of the corresponding MgO and CoO diffraction maxima. The lattice parameters of the spinel and solid solution phases were calculated from the positions of the diffraction maxima.

The average particle sizes were determined from the broadening of the diffraction maxima using the Scherrer equation [14]:

$$d = \frac{0.9\lambda}{B \cos \theta}, \quad (4)$$

where d is the particle size (nm), $\lambda = 0.1789$ nm is the wavelength, B is the full width at half maximum of the peak (rad), and θ is the diffraction angle ($^{\circ}$).

Mössbauer spectra were recorded at 293 K on an MS1104Em spectrometer (CJSC Kordon, Rostov-on-Don, Russia) in transmission mode. A ^{57}Co source in a Rh matrix with an activity of 100 mCi was used. The spectral analysis included determination of the isomer shifts I_s (mm s^{-1}) relative to $\alpha\text{-Fe}$, quadrupole splitting Q_s (mm s^{-1}), effective magnetic field H_{eff} (kOe), and relative areas of the spectral components S (%). The uncertainties of the determined parameters were $\Delta I_s = \pm 0.03 \text{ mm s}^{-1}$, $\Delta Q_s = \pm 0.03 \text{ mm s}^{-1}$, $\Delta H_{\text{eff}} = \pm 5 \text{ kOe}$, and $\Delta S = \pm 2\text{--}3\%$.

FTIR spectra were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Milan, Italy) at room temperature in the range of $4000\text{--}400 \text{ cm}^{-1}$ in transmission mode. The samples for analysis were prepared by pressing with KBr.

The surface morphology and elemental composition of the samples were studied by scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM–EDS). The measurements were performed on a JSM–6610LV scanning electron microscope (JEOL, Akishima, Tokyo, Japan) equipped with an INCA Energy 450 EDS system (Oxford Instruments, Oxford, UK). EDS mapping was used to evaluate the distribution of elements in the samples. The spatial correlation of elemental distributions was quantified from the elemental maps by calculating Pearson correlation coefficients R using Wolfram Mathematica v. 13.3.1.0 software (Wolfram Research, Champaign, IL, USA).

Temperature-programmed oxygen desorption (O_2 -TPD) was carried out using a custom-built setup with analysis of the gas flow on a Chromatek–Crystal 5000 gas chromatograph (Chromatek, Yoshkar-Ola, Russia). A thermal conductivity detector was used. Desorption was performed in a He flow of $30 \text{ cm}^3 \text{ min}^{-1}$; the sample weight was 100 mg. The samples were heated from room temperature to $1100 \text{ }^{\circ}\text{C}$ at a rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ and held at $1100 \text{ }^{\circ}\text{C}$ for 40 min.

5. Conclusions

In this work, phase formation in a Co–Mg–Fe oxide system obtained by thermal decomposition of nitrate precursors with a Co:Mg:Fe ratio of 1:1:1 was studied over a wide range of heat treatment temperatures. The results show that the phase composition of the system changes in stages and can be divided into a low-temperature region up to and including $800 \text{ }^{\circ}\text{C}$, and a high-temperature region formed at $900 \text{ }^{\circ}\text{C}$ and above.

According to X-ray diffraction (XRD) and Mössbauer spectroscopy, at $400 \text{ }^{\circ}\text{C}$ the system contains $\alpha\text{-Fe}_2\text{O}_3$, including Mg-modified state, cobalt-containing spinel phases, and a rocksalt oxide phase. Starting from $550 \text{ }^{\circ}\text{C}$, a ferrite spinel phase is formed, and

its relative content increases with increasing temperature. The transition through the 800–900 °C region is accompanied by the disappearance of cobalt-containing spinel phases, a sharp change in the inversion parameter of the mixed ferrite, and the formation of a stable high-temperature combination of ferrite spinel and rocksalt oxide solid solution.

Mössbauer spectroscopy showed that the transformations of iron-containing components are associated not only with changes in phase composition, but also with changes in the local environment of Fe^{3+} and redistribution of cations between the A and B sublattices of the ferrite spinel. Fourier-transform infrared (FTIR) spectroscopy confirmed rearrangement of the Me–O bonds during the transition from the low-temperature to the high-temperature region, in particular the disappearance of the high-frequency band near 660 cm^{-1} associated with the decomposition of cobalt-containing spinel phases.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that increasing heat treatment temperature leads to coarsening of aggregates and development of sintering features; however, the material retains a granular morphology. Correlation analysis of elemental maps indicates spatial correlation of Co-, Mg-, and Fe-containing components after heat treatment at 550–650 °C and above, confirming that the components remain closely distributed despite the multiphase nature of the system.

Temperature-programmed oxygen desorption (O_2 -TPD) data indicated that the largest amount of oxygen capable of being released upon heating is characteristic of the low- and medium-temperature samples containing cobalt-containing spinel and mixed oxide components. After transition to the high-temperature region, the amount of desorbed oxygen decreases significantly, which is associated with decomposition of cobalt-containing spinel phases, crystallite growth, and formation of a more stable ferrite–oxide system.

The low-temperature region, up to 800 °C, is characterized by pronounced changes in the occupancy of the A and B sublattices by metal cations and by an increase in the inversion parameter. The sharp decrease in the inversion parameter in the 800–900 °C region can be related to the decomposition of cobalt-containing spinel phases and the appearance of additional CoO- and MgO-containing components, accompanied by rearrangement of the cation distribution in the ferrite phase. With a further increase in temperature, the inversion parameter growth may reflect continued cation exchange between the A and B sublattices, caused by increased cation mobility and, possibly, by an increased contribution of configurational entropy to the high-temperature cation distribution. Thus, in the low-temperature range of 400–800 °C, the system contains hematite, cobalt oxide, and cobalt spinel phases, which may provide structural prerequisites for catalytic activity in deep oxidation reactions at these temperatures. At temperatures above 800 °C, cobalt oxide, magnesia, and ferrite phases are present in the system and provide structural prerequisites for catalytic activity in high-temperature oxidation processes.

Overall, the combined XRD, Mössbauer spectroscopy, FTIR, SEM/EDS, and O_2 -TPD results show that heat treatment in air leads to the formation of a multiphase Co–Mg–Fe oxide system combining cobalt-containing spinel phases, ferrite spinel, and Co–Mg-containing rocksalt oxide components. Therefore, the obtained data confirm the possibility of using iron-containing components in the synthesis of deep oxidation catalysts, with the system composition potentially relevant for oxidation catalysis over a wide heat-treatment temperature range. The system's structural features may be relevant for the development of thermally stable oxidation catalysts, with direct evaluation of catalytic behavior requiring further analysis under reducing and reaction atmospheres.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16070652/s1>, Figures S1–S9: elemental mapping of the Co–Mg–Fe samples after heat treatment at 400–1300 °C; Table S1: lattice parameters of the crystalline

phases in the Co–Mg–Fe samples calcined at different temperatures; Table S2: average particle sizes of the crystalline phases in the Co–Mg–Fe samples calcined at different temperatures.

Author Contributions: Conceptualization, A.S. and I.T.; methodology, A.B.; software, B.K.; validation, R.Y. and V.Y.; formal analysis, K.R.; investigation, K.R. and R.Y.; resources, A.K.; data curation, V.Y.; writing—original draft preparation, A.S. and I.T.; writing—review and editing, A.B.; visualization, A.K.; supervision, B.K.; project administration, A.B.; funding acquisition, B.K. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CMF	Co–Mg–Fe oxide system
EDS	Energy-dispersive X-ray spectroscopy
FTIR	Fourier-transform infrared spectroscopy
PDF	Powder Diffraction File
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TPD	Temperature-programmed desorption
XRD	X-ray diffraction

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