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In situ Study of Reduction of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ Mixed Oxides: the Role of Manganese Content

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ABSTRACT: A series of Mn-Co mixed oxides with a gradual varying of the Mn/Co molar ratio was prepared by coprecipitation of cobalt and manganese nitrates. The structure, chemistry, and

reducibility of the oxides were studied by X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (TPR).

It was found that at concentrations of Mn below 37 at%, a solid solution has a structure of a cubic spinel. At concentrations above 63 at.%, a solid solution is formed on the basis of the tetragonal spinel, while at the concentrations in a range 37–63 at.%, a two-phase system, which contains tetragonal and cubic oxides, is formed. To elucidate the reduction route of mixed oxides, two approaches were used. First of them was based on a gradual change in the chemical composition of Mn-Co oxide illustrating the slow changes in the TPR profiles. The second approach consisted in the combination of *in situ* XRD and *pseudo in situ* XPS techniques, which made it possible to directly determine the structure and chemistry of the oxides under reductive conditions. It was shown that the reduction of Mn-Co mixed oxides proceeds via two stages. During the first stage, $(\text{Mn,Co})_3\text{O}_4$ is reduced to $(\text{Mn,Co})\text{O}$. During the second stage, solid solution $(\text{Mn,Co})\text{O}$ is transformed to metallic cobalt and MnO. The introduction of manganese cations into the structure of cobalt oxide leads to a decrease in the rate of both reduction stages. However, the influence of additional cations on the second reduction stage is more noticeable. This is due to crystallographic peculiarities of the compounds: the conversion from the initial oxide $(\text{Mn,Co})_3\text{O}_4$ into the

intermediate oxide (Mn,Co)O requires only a small displacement of cations, whereas the formation of metallic cobalt from (Mn,Co)O requires a rearrangement of the entire structure.

1. INTRODUCTION

The reduction of metal oxides is one of the most important issues of solid-state chemistry, which includes investigations of chemical and phase transformations during oxygen removal (for example, under H₂, CO, or CH₄ flows or interacting with liquid and solid reagents). A detailed knowledge of the reducibility of oxides is important not only from a fundamental point of view; it is also widely used in industries such as metallurgy, catalysis, and electronics. The reducibility of oxides is an essential characteristic of catalysts used in many different reactions. First, it is important for oxidation reactions following the Mars-van Krevelen mechanism¹⁻⁴, in which mobile lattice oxygen of transition metal oxides takes part in the oxidation of reactants. In this case, the reducibility of the oxide catalyst determines the tendency of the oxide to lose oxygen or to donate it to substrates. Second, the oxide reduction can be an activation stage of the Fischer-Tropsch synthesis⁵⁻⁸, water-gas shift reaction⁹⁻¹¹, and oxidative dehydrogenation of hydrocarbons^{12, 13}. In this case, the activation of catalysts leads to the transformation of active species from an oxidized state to the metallic state, and depending on the reductive conditions, the active states can be

changed drastically. Third, under reductive conditions, it is possible to create unique types of active states of catalysts due to nanoparticle exsolution onto the surface of mixed oxides^{14, 15}.

The reduction of simple oxides, such as Fe_2O_3 , NiO , CuO , Co_3O_4 , and Mn_3O_4 , has been widely studied¹⁶⁻²². In contrast, in the case of mixed oxides, there is lack of understanding. In general, the presence of two metals in the oxide structure can lead to the formation of new intermediate oxides during the reduction. Moreover, the introduction of an additional element can lead to slowdown or acceleration of chemical reactions and to the appearance of cations in unusual coordinations. In this work, we studied the effect of doping of cobalt oxide with manganese cations on its reducibility. Co-Mn mixed oxides demonstrate a high catalytic activity in the oxidation of CO²³⁻²⁵ and volatile organic compounds^{26, 27}; they are employed also in bifunctional electrocatalysts²⁸ and as precursors of catalysts for the Fischer-Tropsch synthesis²⁹⁻³¹. Understanding the pathways of reduction and the influence of additives will help to improve the catalytic performance and elucidate the nature of the active sites. The knowledge of the reduction of mixed Mn-Co oxides is rather scarce, and most of it is focused on studies of supported catalysts^{8, 27, 32, 33}. Previously, we have investigated structural transformations occurring during the reduction of a two-phase system consisting of MnCo_2O_4 and CoMn_2O_4 with a total molar ratio Mn : Co = 1 : 1 in comparison with

the simple oxides Co_3O_4 and Mn_3O_4 ³⁴. Herein, the reduction of a series of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ solid solutions with a gradual variation in the chemical composition was studied *in situ* by XRD, XPS, and TPR.

2. EXPERIMENTAL SECTION

Samples with the different Co:Mn molar ratio were prepared by the coprecipitation method. A calculated amount of $\text{Co}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ aqueous solutions was poured into a round-bottom flask. Precipitation was carried out under stirring with a gradual addition of a NaOH solution to bring pH of the solution to 11. After subsequent aging, the precipitate was filtered, washed with distilled water on a filter to pH = 6, and dried at 120 °C. Then the sample was calcined in air at 600 °C for 4 h. The resulting samples were referred to as $\text{Mn}_x\text{Co}_{3-x}$ ($x=0.1-2.9$), where $x/(3-x)$ is the ratio between Mn and Co cations.

The phase composition of fresh samples was studied by XRD using a Thermo X'tra diffractometer. The diffraction patterns were obtained in the 2θ range from 15° to 70° with a step of 0.05° using the Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The phases were identified using the powder diffraction database PDF-4+. The quantitative phase analysis was performed by the Rietveld method using the TOPAS program. The instrumental broadening was described with metallic

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4 silicon as a reference material. The coherent scattering region (CSR) was calculated using LVol-
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7 IB values (i.e. volume averaged column height calculated from the integral breadth).
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10 The chemical composition of the oxides was analyzed by X-ray absorption near edge structure
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12 (XANES) spectroscopy. The experiments were performed at the P65 beamline ³⁵ at the
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14 synchrotron radiation facility PETRA III (DESY, Hamburg, Germany). The electron storage ring
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17 of PETRA III was operating at 6 GeV in the top-up mode keeping the electron current stable within
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20 1%. The synchrotron radiation was provided by an 11-period undulator. The radiation was
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The XANES data were processed according to standard procedures with the ATHENA program of the IFEFFIT software package ³⁶.

The temperature-programmed reduction in hydrogen (TPR-H₂) was performed with 40-60 mg of a sample in a quartz reactor using a flow setup with a thermal conductivity detector. The reducing mixture contained 10 vol.% of H₂ in Ar was passed through the setup with a constant

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4 flow rate near 40 ml/min. The rate of heating from room temperature to 900 °C was approximately
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7 10°C/min.
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10 *In situ* XRD experiments were also performed at the P65 beamline. The reduction was studied
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13 under a flow 10% H₂ in helium with the flow rate of 10 mL/min. The sample was loaded into a
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16 quartz capillary, allowing gas to pass through the sample volume. The capillary temperature was
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19 increased from 25 to 600 °C with a heating rate of 10°C/min using a calibrated gas blower. The
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22 energy of synchrotron radiation was 20 keV, the beam size was 1.0 mm × 1.2 mm. XRD patterns
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25 were recorded using an XSpecrum Lambda 750k detector. The accumulation time was 1 min per
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28 scan. Corundum was used as a standard.
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33 In addition, the reduction of the *Mn_{2.5}Co_{0.5}* sample was studied by XPS. The experiments were
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36 performed using an X-ray photoelectron spectrometer (SPECs Surface Nano Analysis GmbH,
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39 Germany) equipped with an XR-50M X-ray source, a FOCUS-500 X-ray ellipsoidal
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42 monochromator, a PHOIBOS-150 hemispherical electron energy analyzer, and a high-pressure
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45 cell (HPC). To elucidate the reduction process, the sample was treated in hydrogen at 150, 250,
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48 300, and 400 °C. Each treatment was performed in the HPC at atmospheric pressure for 30 min.
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52 After the treatment, the sample was cooled to room temperature, the HPC was pumped out, and
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the sample was transferred to the analytical chamber without contact with air, where the $\text{Co}2p$, $\text{Mn}2p$, $\text{C}1s$, and $\text{O}1s$ core-level spectra were recorded under ultrahigh vacuum conditions. This allowed us to “freeze” a reduced state formed after the treatment at atmospheric pressure and to study in detail the reduction process using the convenient XPS apparatus. This approach is referred to as a pseudo in situ XPS study³⁷. The core-level spectra were obtained using the monochromatic Al $\text{K}\alpha$ radiation ($h\nu = 1486.74 \text{ eV}$). The charge correction was performed by setting the $\text{C}1s$ peak at 284.8 eV . Relative concentrations of elements were determined from the integrated intensities of the core-level spectra using the cross sections according to Scofield³⁸. For detailed analysis, the spectra were fitted into several peaks after the background subtraction by the Shirley method. The fitting procedure was performed using the CasaXPS software³⁹. The line shape of the peaks was approximated by the multiplication of the Gaussian and Lorentzian functions.

3. RESULTS

Structure and Chemistry of As-prepared Samples. Figure 1a shows X-ray diffraction patterns of $\text{Mn}_x\text{Co}_{3-x}$ with x varying from 0.1 to 2.9. For $x = 0.1$, the XRD pattern corresponds to Co_3O_4 -like oxide with the cubic spinel structure [space group $Fd\bar{3}m$, PDF No 00-043-1003]. With an increase in the Mn content, the diffraction reflections broaden and shift toward the lower angular

region. For $x = 1.3$, the XRD pattern exhibits additional peaks at $2\theta = 29.3^\circ$, 31.1° , 33.2° , 44.8° , 52.2° , and 60.8° , which belong to the tetragonal spinel of the Mn_3O_4 -type structure [space group $I4_1/amd$, PDF No 00-024-0734]. For $x = 1.3$ -1.7, a two-phase pattern is observed. The phase quantification by the Rietveld refinement is shown in Figure 1b. As seen, an increase in the Mn content leads to a gradual decrease in the amount of the cubic phase and an increase in the tetragonal oxide content. For $x > 1.7$, the diffraction patterns exhibit only reflections of the tetragonal phase of the Mn_3O_4 type (Figure 1a).

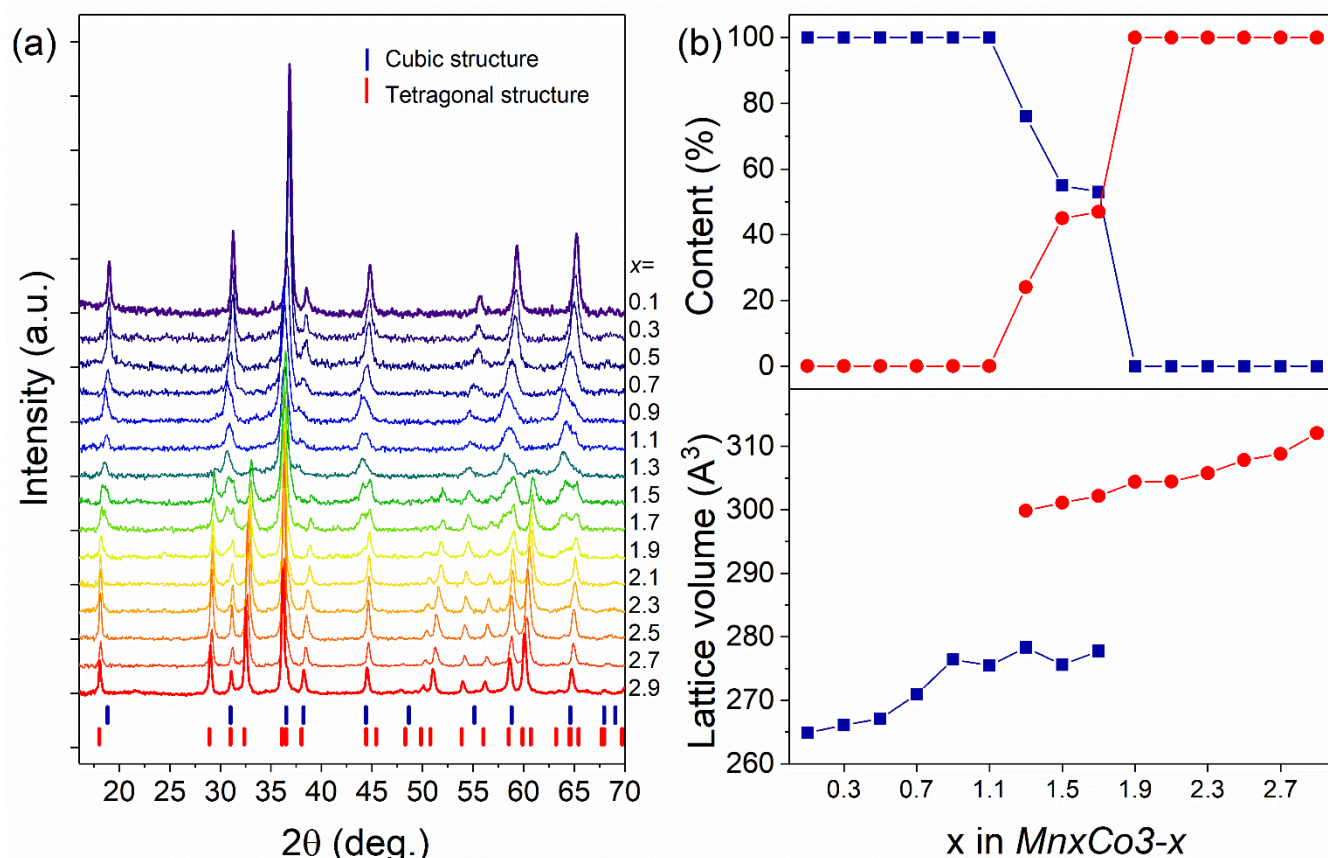


Figure 1. XRD patterns of the $MnxCo3-x$ samples (a); the red bar chart indicates the reflections of tetragonal spinel [Mn_3O_4 , PDF No 00-024-0734], the blue bar chart indicates cubic spinel [Co_3O_4 , PDF No 00-043-1003]. Normalized lattice volume, content of cubic (blue squares) and tetragonal (red circles) spinels in dependence on the Mn content (x) in $MnxCo3-x$ sample (b).

As known, Co_3O_4 has the structure of cubic spinel with the $Fd\bar{3}m$ space group and is characterized by 8 formula units, while Mn_3O_4 forms the tetragonal spinel ($I4_1/amd$), which contains 4 formula units. Since the structures of tetragonal and cubic spinels contain a different number of formula units, for a convenient comparison of the lattice parameters of mixed oxides, we used the normalized volume V^* of the unit cell. For the cubic oxide, the volume is calculated as $V^* = a^3/2$, and for the tetragonal oxide, the volume is calculated as $V^* = a^2 c$. Figure 1b shows the normalized volume for the mixed Mn-Co oxides in dependence on the Mn content (x) in sample. As seen, the normalized lattice volume gradually increases with increasing x from 0.1 to 0.9. In the range of x from 1.3 to 1.7, the volume changes sharply, which is associated with the appearance of the tetragonal phase. Since the ionic radius of manganese is larger than that of cobalt ($r = 0.58 \text{ \AA}$, CN = 6 for Mn^{3+} , $r = 0.55 \text{ \AA}$, CN = 6 for Co^{3+} ; $r = 0.56 \text{ \AA}$, CN = 4 for Co^{2+} ⁴⁰), the increase in the normalized volume indicates the incorporation of manganese into the oxide

structure with the formation of solid solutions. From $x = 0.1$ to $x = 0.9$, manganese cations are gradually introduced into the Co_3O_4 structure. For $x = 0.9$ -1.7, the change in the cubic lattice volume is insignificant, and $V^* = 276.3$ -278.3 \AA^3 (Table S1), which is close to value for the Co_2MnO_4 oxide ($V^* = 282.7 \text{ \AA}^3$ for Co_2MnO_4 [PDF No 00-023-1237]). From $x = 1.3$ to $x = 2.9$, the volume of the tetragonal phase increases from 299.9 to 311.9 \AA^3 , which corresponds to an increase in the concentration of manganese cations in the solid solution. The increase in x is accompanied by a gradual decrease in the CSR of the cubic oxide from 220 to 80 \AA and by an increase in the CSR of the tetragonal phase from 100 to 260 \AA (Table S1). With the addition of a dopant, the microstrains increase from 0.12% to 0.45% and from 0.04% to 0.17% for cubic and tetragonal oxides, respectively. During the formation of solid solutions, an increase in microstrains is observed due to the difference in the atomic radii of the elements. In fact, geometrically different atoms are located in crystallographically equivalent positions, which leads to deformations. An increase in stresses leads to a loss of long-range order in the arrangement of atoms, and thus to decrease in the CSR.

During the formation of solid solutions, a change in the crystalline size of particles often occurs in comparison with simple oxides. The introduction of the second element can lead to a change in

microstructural characteristics, both due to interaction at the atomic level, i.e. the formation of solid solutions, and mechanically preventing, for example, the crystallization of the compound when the modifier is in the form of individual particles or within the grain boundaries.

The Mn K-edge XANES spectra of the $MnxCo_{3-x}$ samples for $x = 0.1, 0.3, 0.7, 1.1, 1.9, 2.3, 2.5,$ and 2.7 (Figure 2a) as well as the spectra of standard Mn-based materials (Figure 2b) were obtained to elucidate the chemical state of manganese cations in the mixed oxides. The Mn K-edge XANES spectra contain two regions: the main peak of the K-edge absorption due to the $1s \rightarrow 4p$ transition (peak C in Figure 2a) and the pre-edge region (peaks A_1 and A_2 in Figure 2a) due to the $1s \rightarrow 3d$ transitions, which represent electronic and structural features. At the absorption edge, the inflection point contains a shoulder (B). As shown in the inset in Figure 2a, the pre-edge region is characterized by a splitting of 3d orbitals into t_{2g} and e_g orbitals. The relative increase in the A_2 peak intensity indicates an increase in the number of unoccupied e_g orbitals in the $1s \rightarrow 3d$ quadrupole-allowed transition, which is in agreement with the increased Mn^{4+}/Mn^{3+} ratio in the manganese oxides^{41, 42}.

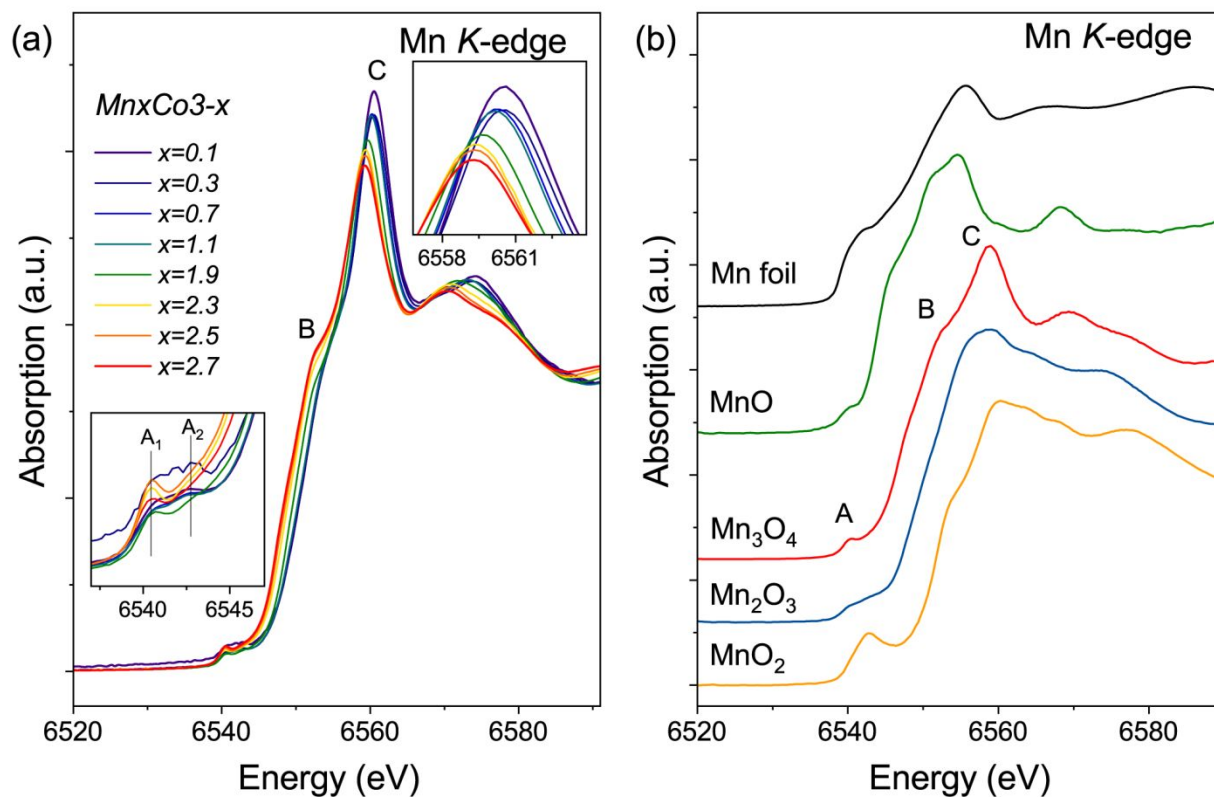


Figure 2. Normalized Mn *K*-edge XANES spectra of the Mn_xCo_{3-x} samples for $x = 0.1, 0.3, 0.7, 1.1, 1.9, 2.3, 2.5,$ and 2.7 (a) and $MnO_2, Mn_2O_3, Mn_3O_4, MnO,$ and Mn foil (b).

The Mn absorption edge of the Mn_xCo_{3-x} samples with $x = 2.7-2.3$ is similar to that of Mn_3O_4 . The shift of the absorption edge toward that of MnO_2 with decreasing x shows that Mn is further oxidized during the substitution of Mn by Co. Simultaneously, the intensity of the A_2 peak in the pre-edge region (the inset in Figure 2a) decreased slightly with increasing x in the Mn_xCo_{3-x} samples, indicating the reduction of Mn^{4+} cations to Mn^{3+} .

XANES is an effective tool for determining the average oxidation states of an absorbing element in a sample ^{43, 44}. It is known that the main edge shifts to higher energies with an increase in the oxidation state of Mn. There is a nearly linear relationship between edge-energy positions and formal oxidation state of Mn in the series of Mn-oxides. XANES edge-energy varies by a few electron volts from sample to sample, in part because it depends on oxidation state averaged for all the Mn atoms in the sample. ⁴⁵ Besides, ligands bound to the absorbing element also contribute to the general shape of the edge and apparent edge energy. ^{46, 47} As a result, this correlation between edge-energy and an element's formal oxidation state is purely empirical and definition of the specific oxidation state of the element at each site is complicated. ^{48, 49}

The Mn K-edge XANES spectra of bulk manganese oxides (Figure 2b) were used to determine the correlation between the absorption edge position and the oxidation state of manganese. Figure 3 shows a linear dependence of the oxidation state of Mn on the position of the K-edge in the series of manganese oxides: MnO (Mn²⁺), Mn₃O₄ (Mn^{2.66+}), Mn₂O₃ (Mn³⁺), and MnO₂ (Mn⁴⁺) ⁵⁰⁻⁵⁵. The absorption edge of manganese in the metallic state is at 6539 eV ⁵⁶. The absorption edge for the *MnxCo3-x* oxides shifts with the Mn content (Figure 3, red circles).

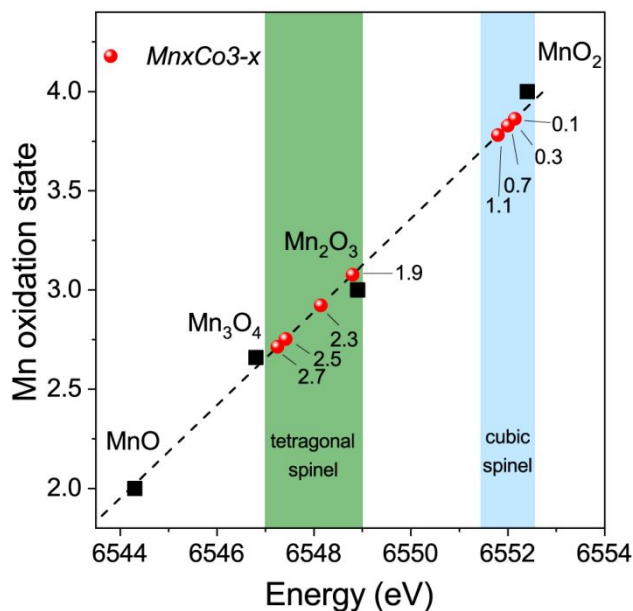


Figure 3. Calibration curves for XANES analysis determined using manganese oxides as references. Red circles indicate experimental data for the Mn_xCo_{3-x} samples (numbers near the red circles indicate the value of x). Black squares correspond to reference oxides.

The absorption edge of the $Mn_{2.7}Co_{0.3}$ sample at $E = 6547.25$ eV corresponds to the charge state of $2.71+$. With a decrease in the Mn content from $x = 2.7$ to $x = 1.9$, the energy of the absorption edge increases to 6548.80 eV, corresponding to Mn in the charge state of $3.08+$. With a further decrease in the manganese content, the space group changes from tetragonal $I4_1/amd$ ($x = 2.7-1.9$) to cubic $Fd\bar{3}m$ ($x = 1.1-0.1$). As seen, the absorption edge sharply shifts from 6548.80 eV ($x = 1.9$) to 6551.80 eV ($x = 1.1$). Hence, we can speculate that the average oxidation states for

the cubic oxides are higher than that for the tetragonal modification. According to the calibration curve, a decrease in x from 1.1 to 0.1 leads to a growth of the oxidation state of Mn cations from 3.78+ to 3.86+.

The Co K-edge XANES spectra are shown in Figure 4. In the case of Mn_xCo_{3-x} ($x = 0.1-1.1$), the spectra have similar shape to Co_3O_4 , and cobalt cations have the oxidation state near 2.6+.⁵⁷ When the Mn content increases from 1.1 to 2.7, the main peak of the XANES spectra shift from 7729 to 7731.7 eV 7731.5 to 7731.0 eV and its intensity gradually decreases, indicating a lower oxidation state of Co at a lower Co content. Similar results have been obtained in other spinel Co-Mn system.⁵⁰ A lower Co valence value tends to appear in oxides with lower Co content, suggesting an increase in the ratio of Co^{2+}/Co^{3+} due to substitution of Mn cations.⁵⁸ The Co K-edge XANES spectra exhibit some changes in the shape of the edge as Co is substituted by Mn due to changes in the local environment of Co. However, they do not show a steady shift to lower energies when the Mn content increases from 0.1 to 1.1 and then from 1.9 to 2.7. Because the energy shift is below 1 eV when x changes in the ranges of 0.1-1.1 and 1.9-2.7, the estimated difference between the oxidation states of cobalt is less than 0.1.¹⁰ However, unlike the shift in the Mn K-edge XANES spectra, a shift of the main absorption peak in the Co K-edge spectra

toward lower energies (≈ 1.0 eV) is evident when x increases from 1.1 to 1.9. This behavior can be explained as due to local environment of cobalt. Cobalt occupies cubic and tetrahedral positions in cubic spinel structure in the case of $MnxCo_{3-x}$ ($x = 0.1-1.1$), while it occupies mainly tetrahedral positions in tetragonal spinel ($x = 1.9-2.7$).

For pure Mn_3O_4 and Co_3O_4 , the average oxidation state of cations is 2.66+. For the tetragonal solid solutions ($x = 1.9-2.7$), the oxidation state of Mn is between 2.71+ and 3.08+, which is close to the theoretical value of 2.7-3 (the theoretical average oxidation state of Mn is calculated from the electroneutrality principle and assumption that $Mn_xCo_{3-x}O_4$ oxide contains Co^{2+} cations for $x \geq 2$). Unfortunately, the exact state of cobalt is difficult to determine. For $x < 1.1$, a cubic spinel is formed, in which the average oxidation state of Mn is greater than 3+. Probably, Mn is partially in the Mn^{4+} state, which is in a good agreement with the literature data for Mn-Co oxide solid solutions ⁵⁹.

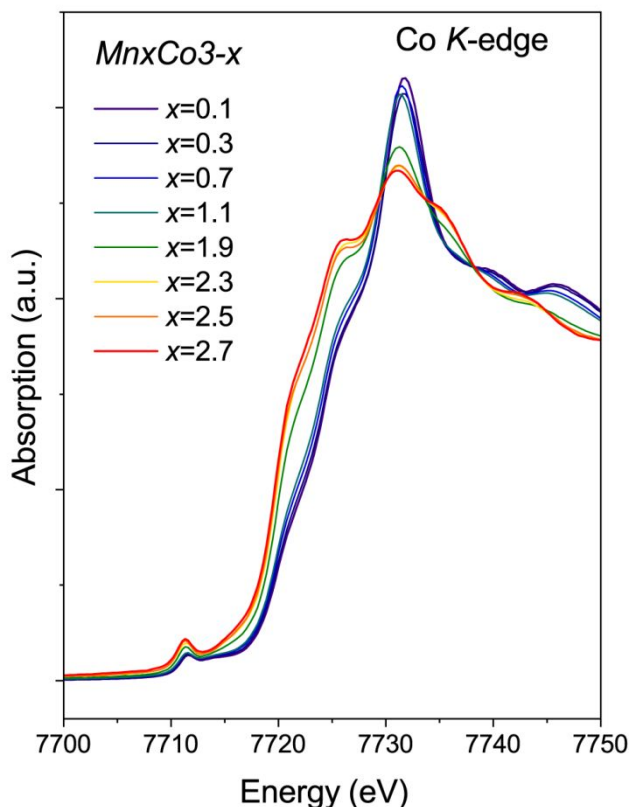


Figure 4. Co *K*-edge XANES spectra of the Mn_xCo_{3-x} samples for $x = 0.1, 0.3, 0.7, 1.1, 1.9, 2.3, 2.5$, and 2.7 .

TPR- H_2 Study. Figure 5a shows TPR curves for Mn_xCo_{3-x} with x varying from 0.1 to 3. As seen, the TPR curve of pure Co_3O_4 ($x = 0$) exhibits two peaks of hydrogen consumption with maxima at 320 °C (A peak) and 370 °C (B peak). The presence of two peaks corresponds to the two-step reduction: $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$ and $CoO + H_2 \rightarrow Co + H_2O$ ^{21,60}. With an increase

in x and with the incorporation of manganese cations into the oxide structure, the following three effects are observed on the TPR curves.

(1) The A peak shifts from 320 to 450 °C, and the B peak shifts from 370 to 875 °C (Figure 5b).

(2) The ratio of the peak intensities changes. The hydrogen consumption increases for the A peak and decreases for the B peak (Figure 5a). The total amount of consumed hydrogen decreases from 17.3 to 5.33 mmol H₂/g due to the reduction of cobalt oxide to Co⁰ and manganese oxide to Mn²⁺.

(3) There appear small low-temperature peaks. Probably, they are associated with the reduction of amorphized or highly dispersed oxides, which are undetectable by XRD.

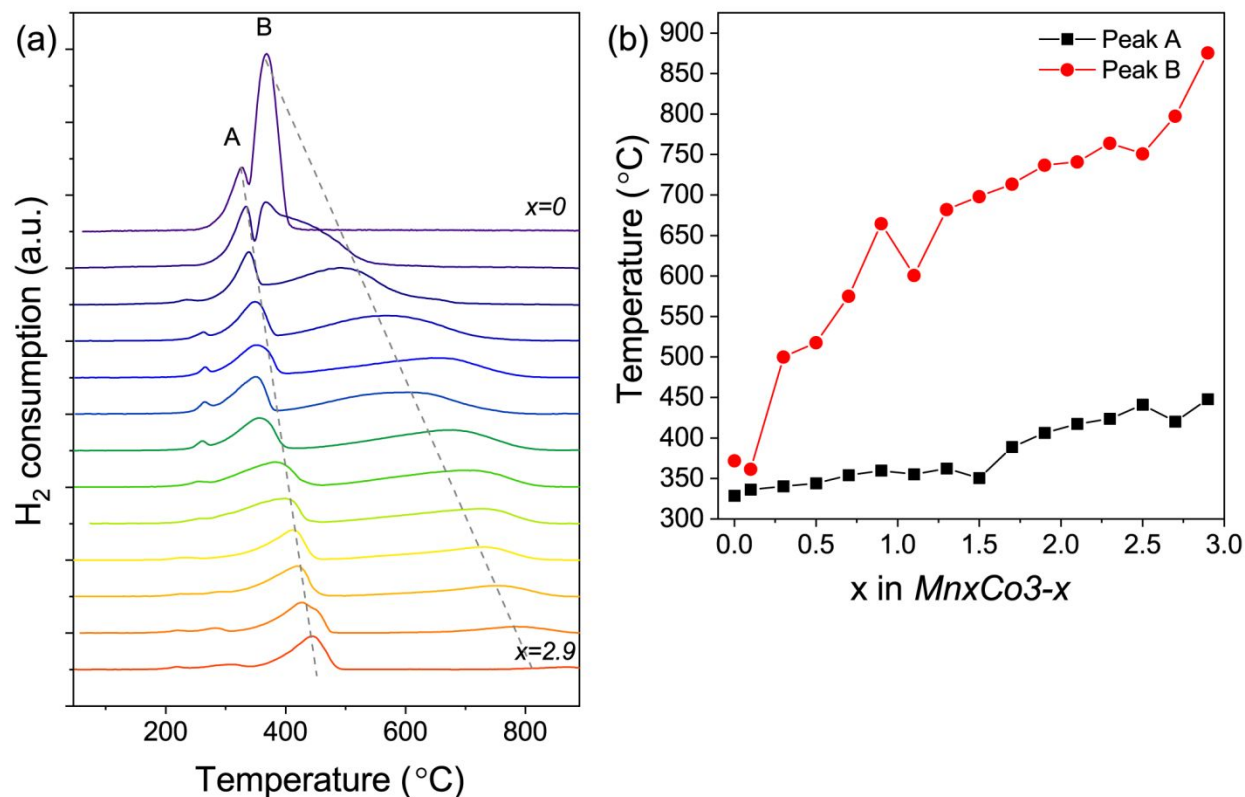
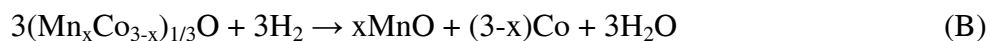
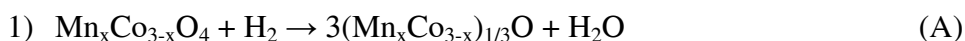
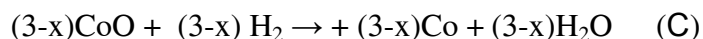
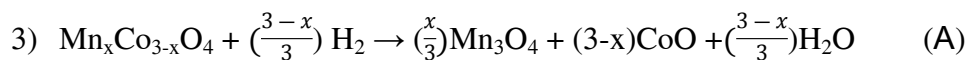
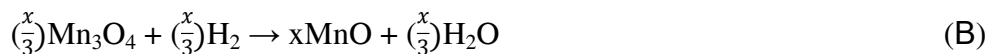
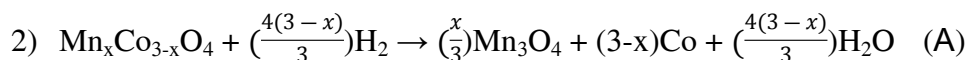


Figure 5. TPR- H_2 profiles of Mn_xCo_{3-x} samples with x increasing from 0 to 2.9 (a). Position of A and B peaks in dependence on the Mn content (b).

The following reaction pathways of the reduction of $Co_{3-x}Mn_xO_4$ can be considered: (1) the reaction proceeds through the formation of the mixed oxide $(Mn_xCo_{3-x})_{1/3}O$, (2) the release of Co from the structure of the $Co_{3-x}Mn_xO_4$ solid solution, (3) the formation of CoO.





All the proposed reaction routes are characterized by two or three stages, indicating that there are several peaks of the hydrogen consumption on the TPR curves. The intensity of A and B (C) peaks depends on x and the reaction route. Figure 6 illustrates a theoretical dependence of the relative amount of the hydrogen consumption at stage A on the Mn content x (the ratio between the integrated peak area of the A peak and the total amount of consumed hydrogen). For the 1st reaction route, the consumption at stage A rises with increasing x . In the case of the 2nd and 3rd pathways, another dependence is observed: the amount of hydrogen for stage A declines with an increase in x . The experimental data are also shown in Figure 6 (blank hexagons). As seen, the experimental dependence agrees well with the first reaction route, i.e., the reduction of a solid solution proceeds through the formation of the $(\text{Mn}_x\text{Co}_{3-x})_{1/3}\text{O}$ intermediate. To confirm these

assumptions further, we applied *in situ* XRD and XPS techniques to study the chemical state of cations and the crystal structure of Mn-Co oxide solid solutions under a hydrogen flow.

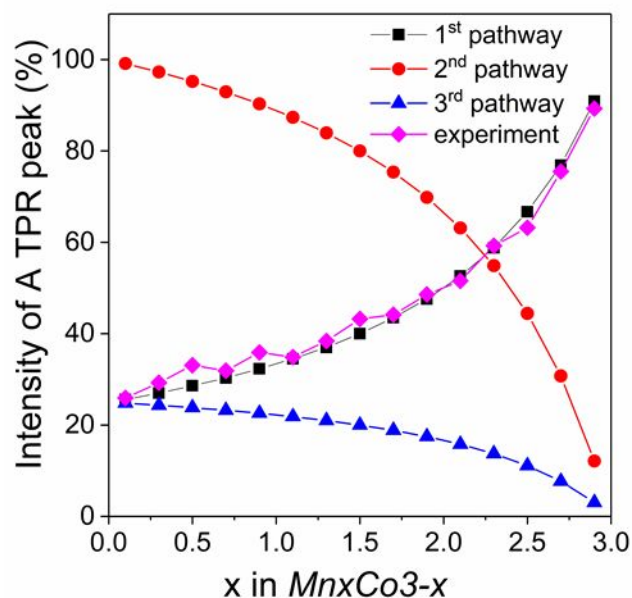


Figure 6. Relative intensity of the A peak in dependence on Mn content (x) in Mn_xCo_{3-x} for three theoretical reaction pathways (squares – 1st, circles – 2nd, triangles – 3rd and diamonds – experimental data)

***In Situ* XRD Study.** The phase transformations that occur during the reduction of Mn_xCo_{3-x} have been further studied by *in situ* XRD (Figure 7, Figures S1-S5). In these experiments, the XRD patterns were collected during heating the samples in the H_2/He mixture from room temperature to 600 °C with a ramp of 10°C/min. The results of the investigation of $Mn_{0.7}Co_{2.7}$ are presented

in Figure 7. At room temperature, the sample consists of cubic spinel $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$. At 250 °C, the intensity of spinel reflections declines, and wide peaks appear at $Q = 2.56, 2.91, 4.12, 4.80, 4.97 \text{ \AA}^{-1}$, which correspond to reflections of a (Co,Mn)O-like oxide [CoO, PDF No 00-042-1300]. At 450 °C, new peaks appear at $Q = 3.06$ and 3.51 \AA^{-1} , which are attributed to 111 and 200 reflections of metallic cobalt (fcc) [Co, PDF No 00-015-0806], and the intensity of a (Co,Mn)O-like intermediate compound decreases. At 450–600 °C, there appear reflections of metallic Co and the (Co,Mn)O-like oxide.

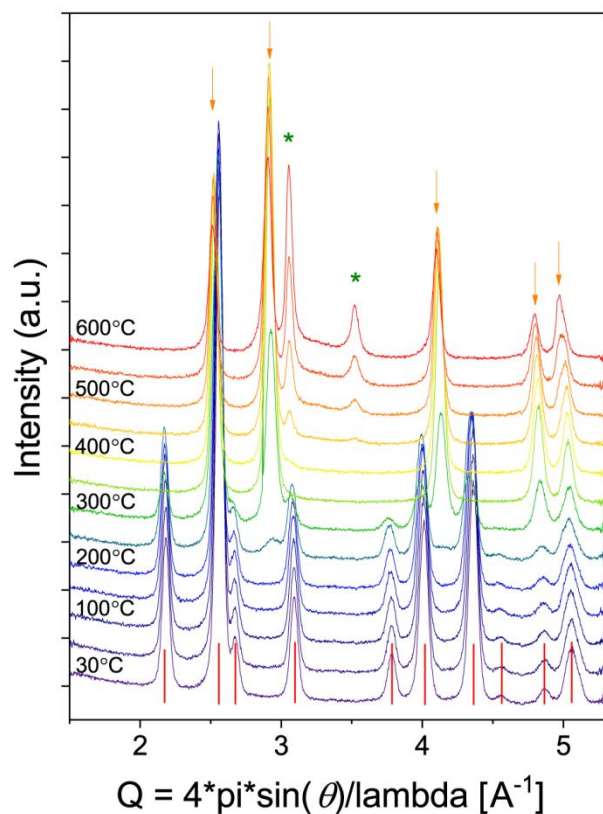


Figure 7. *In situ* XRD patterns of $Mn_{0.7}Co_{2.3}$ collected during heating from 30 to 600 °C in a flow of 10% H_2 in He gas mixture. Lines indicate the position of $Mn_{3-x}Co_xO_4$ cubic spinel reflections, arrows indicate the (Co,Mn)O-like oxide, and the asterisks indicate Co in the metallic state.

Figure 8 summarizes the results of the *in situ* XRD data and shows the temperature ranges for the existence of different phases during the reduction of Mn_xCo_{3-x} samples with $x = 0.1, 0.7, 1.1, 1.9, 2.3,$ and 2.7 . It is worth noting that for the samples with $x = 1.9, 2.3$, the $CoMnO_3$ phase is observed in the initial state (14 wt % and 5 wt % for $x = 1.9$ and 2.3 , respectively). Reflections of this phase are undetectable with the laboratory diffractometer (Figure 1a) because of insufficient intensity of the incident beam, in contrast to the synchrotron radiation. During the reduction, $CoMnO_3$ disappears at 270-300 °C. All the compositions undergo the following transformations:

$$Mn_xCo_{3-x}O_4 \rightarrow (Mn_xCo_{3-x})_{1/3}O \rightarrow Co + MnO.$$

With an increase in the Mn content from $x = 0.1$ to $x = 2.7$, the formation temperature of the intermediate oxide (Mn,Co)O rises from 250 to 300 °C. In addition, the rise in x from 0.1 to 2.3 leads to an increase in the formation temperature of metallic cobalt from 340 to 550 °C. These results are in good agreement with the TPR data (Figure 6). The

addition of Mn slows down the transformations in the initial spinel and stabilizes the intermediate compound (Mn, Co)O oxide.

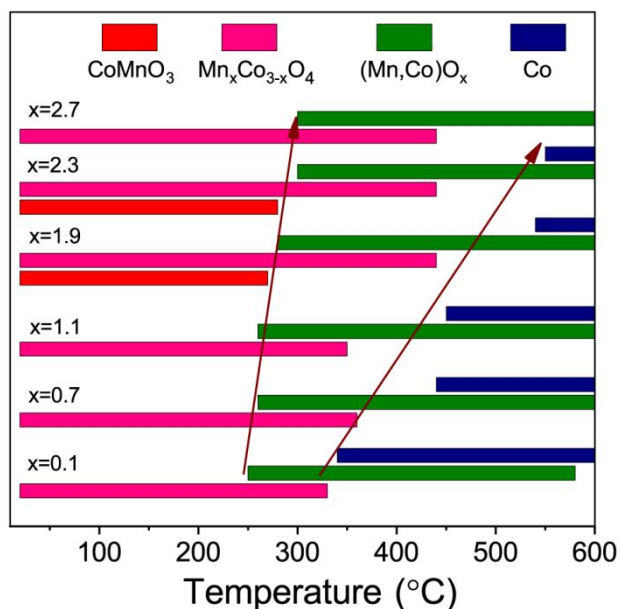


Figure 8. Phase composition of Mn_xCo_{3-x} ($x = 0.1, 0.7, 1.1, 1.9, 2.3$, and 2.7) as a function of reduction temperature.

The TPR and *in situ* XRD data testify to a two-stage reduction process through the formation of an intermediate compound $(Mn_xCo_{3-x})_{1/3}O$, which is consistent with our previous studies³⁴. The gradual introduction of manganese cations into the cobalt oxide structure slightly increases the temperature of the first reduction step and strongly increases the temperature of the second step (the maximum of the first TPR peak shifts from 320 to 450 °C, whereas the maximum of the second

TPR peak shifts from 370 to 875 °C). The presence of Mn and Co cations in one oxide matrix significantly affects the second stage of reduction, but does not influence the first one. Apparently, this is due to the “similarity” of the structures of the initial spinels $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ and $\text{Co}_{1-x}\text{Mn}_x\text{O}$ (rock salt). The spinel consists of a close packing of oxygen, in which cations are located in octahedral and tetrahedral positions, while some of the «non-spinel» octahedral and tetrahedral sites remain empty. The rock salt structure also has a close packing of oxygen, in which cations are located in all octahedral voids. Therefore, for the rearrangement from $(\text{Mn},\text{Co})_3\text{O}_4$ to $(\text{Co},\text{Mn})\text{O}$, it is necessary to move an atom from a tetrahedral position to a neighboring octahedral void. We have previously shown⁶¹ that, during the initial stages of Co_3O_4 reduction, cobalt cations fill the main and additional octahedral positions of spinel, i.e. three filled octahedra are formed, which means the formation of CoO clusters in the Co_3O_4 structure. However, the $\text{CoO} \rightarrow \text{Co}$ transformation requires a complete rearrangement of the structure: oxygen withdrawal, a decrease in the Co-Co distance, and redistribution of atoms. With the introduction of manganese, which retains oxygen more strongly than cobalt (standard electrode potentials are equal to -0.29 and -1.18 eV for $\text{Co}^{2+}/\text{Co}^0$ and $\text{Mn}^{2+}/\text{Mn}^0$, respectively), the exit of cobalt cations from the structure becomes more difficult.

***Pseudo in Situ* XPS Study.** Changes in the chemical state of cations in the *Mn_{2.5}Co_{0.5}* during the reduction by hydrogen were studied using *pseudo in situ* XPS. Table 1 shows relative concentrations (atomic ratios) of elements in the near-surface layer of the sample and the binding energies of Mn $2p_{3/2}$, Co $2p_{3/2}$, and O $1s$ peaks. In the initial state, the atomic ratio [O^{*}]/[Mn + Co] is 1.22, which is close to the stoichiometric value of 1.3 for the spinel structure. During reduction, a gradual decrease in the oxygen content is observed.

Table 1. Atomic ratios of elements, the binding energies of Mn $2p_{3/2}$, Co $2p_{3/2}$, and O $1s$ peaks of *Mn_{2.5}Co_{0.5}* before and after reduction in hydrogen.

Reduction temperature	[Co]/[Mn]	[O ^α]/[Mn + Co]	Mn $2p_{3/2}$			Co $2p_{3/2}$		O $1s$
			Mn ²⁺	Mn ³⁺	Mn ⁴⁺	Co ⁰	Co ²⁺	
fresh	0.128	1.22	640.1	641.5	642.6	–	780.5	529.9 ^α
			(14%)	(68%)	(18%)			531.5 ^β
150 °C	0.154	1.01	640.1	641.5	642.6	–	780.6	529.8 ^α
			(21%)	(67%)	(12%)			531.4 ^β
250 °C	0.200	0.78	640.1	641.6	–	–	780.5	529.6 ^α
			(52%)	(48%)				531.4 ^β
300 °C	0.177	0.81	640.1	641.6	–	–	780.6	529.6 ^α

			(53%)	(47%)				531.4 ^β
			640.1	641.5		778.0	780.4	529.6 ^α
400 °C	0.111	0.75			—			
			(55%)	(45%)		(35%)	(65%)	530.9 ^β

^α oxygen characterized by the O1s binding energy at 529.6-529.9 eV corresponded to the mixed oxide;

^β oxygen corresponded to the OH-groups.

Figure 9a shows the Mn2*p* core-level spectra of the *Mn2.5Co0.5* samples obtained before and after reduction in hydrogen at different temperatures. The shape of Mn2*p* spectra of fresh sample and high binding energy of Mn2*p*_{3/2} peak indicate that manganese in the sample is in the oxidized state. Moreover, analysis of the Mn2*p* core-level spectrum allow us to reveal that manganese presences in the Mn²⁺, Mn³⁺, and Mn⁴⁺ states. Indeed, to identify the chemical state of manganese, the binding energy of Mn2*p*_{3/2} peak, the presence and position of shake-up satellites are used ⁶²⁻⁶⁶. It should be mentioned that there is approach to fit the Mn2*p*_{3/2} peak of individual manganese oxides by several peaks corresponded to Mn cations in the different coordinations and oxide states^{67 63}. To study the reduction of Mn cations we applied the alternative approach – based on our experience of studying the Mn oxides synthesized in the similar conditions and characterized by the other methods we have constructed the peak fitting model for each individual oxide (not presented in this work) and then used the mix of the peak fitting models for fitting the Mn spectra

of samples under study. It allows us to reveal the trend concerning to reduction of Mn cations. The curve-fit analysis of the Mn $2p$ spectra of fresh sample shows that the spectrum is described by three Mn $2p_{3/2}$ -Mn $2p_{1/2}$ doublets and shake-up satellites, which indicates that the as-prepared sample contains Mn $^{2+}$, Mn $^{3+}$, and Mn $^{4+}$ cations (Figure 9a). According to the literature data, manganese in MnO, Mn $_2$ O $_3$, and MnO $_2$ is characterized by the Mn $2p_{3/2}$ binding energy in the ranges of 640.4–641.7, 641.5–641.9, and 642.1–642.6 eV and the spin-energy splitting (ΔE) of Mn $3s$ core-level spectrum is 5.9-6.1, 5.2-5.3, and 4.5-4.7 eV, respectively ⁶²⁻⁶⁶. The spin-energy splitting (ΔE) of Mn $3s$ core-level spectrum for fresh sample is 5.5 eV, that lies between ones corresponded to Mn $^{2+}$ and Mn $^{3+}$ cations. The XPS analysis allows us to estimate the fraction of Mn $^{2+}$, Mn $^{3+}$, and Mn $^{4+}$ cations for fresh sample that is 14%, 68%, and 18%, respectively (Table 1). The presence of Mn $^{4+}$ is likely associated with the oxidation of manganese in the near-surface layers or with the formation of highly dispersed CoMnO $_3$ ⁶⁸. After heating in hydrogen at 150 °C, manganese undergoes partial reduction and the fraction of manganese in the Mn $^{3+}$ and Mn $^{4+}$ states decreases (Table 1) and the spin-energy splitting (ΔE) of Mn $3s$ core-level spectrum increases to 5.6 eV as well. At 250-400 °C, the Mn $2p$ doublet, which could be attributed to manganese in the Mn $^{4+}$ state, does not appear in the spectra, while the fraction of manganese in the Mn $^{2+}$ + state

increases to 55%. And it should be noted that the spin-energy splitting (ΔE) of Mn3s core-level spectrum reaches to 5.9-6.0 eV that lies between ones corresponded to Mn²⁺ and Mn³⁺ cations but it is more closely to the Mn²⁺ state.

The Co2p core-level spectra of *Mn2.5Co0.5* obtained before and after reduction in hydrogen are presented in Figure 9b. The spectra consist of the Co2p_{3/2}-Co2p_{1/2} doublet and corresponded “shake-up” satellites. In case of sample treated in hydrogen at 400°C there is additional Co2p_{3/2}-Co2p_{1/2} doublet with lower Co2p_{3/2} binding energy. To identify the chemical state of cobalt, the position of the Co2p_{3/2} main line, the shape of the Co2p spectrum (the intensity and relative position of the “shake-up” satellites), and the spin-orbit splitting Co2p_{3/2}-Co2p_{1/2} should be used⁶⁹. In the case of *Mn2.5Co0.5*, the Co2p_{3/2} spectra are represented by an asymmetric peak with a binding energy in the range of 780.4–780.6 eV and a broad “shake-up” satellite at 786.6 eV. The spin-orbit splitting of Co2p_{3/2}-Co2p_{1/2} is 15.95 eV. In the spectrum of metallic cobalt Co and the LiCoO₂ and Co₃O₄ oxides, the “shake-up” satellites are not observed, and the Co2p_{3/2} binding energy lies in the range of 778.0–778.2 and 779.5–780.5 eV^{63, 69, 70}. Cobalt in the Co²⁺ state is characterized by Co2p_{3/2} binding energies in the range of 780.0–782.0 and by the presence of an intense “shake-up” satellite in the range of 786–787 eV^{69, 71}. The Co2p_{3/2} binding energy, as well

as the presence of distinct “shake-up” satellites, indicates that cobalt in the $Mn_{2.5}Co_{0.5}$ sample is in the Co^{2+} state both initially and during reduction. The additional $Co2p_{3/2}$ – $Co2p_{1/2}$ doublet with the $Co2p_{3/2}$ binding energy at 778.0 eV observed after reduction at 400 °C corresponds to cobalt in the metallic state. The fraction of metallic cobalt is about 35%.

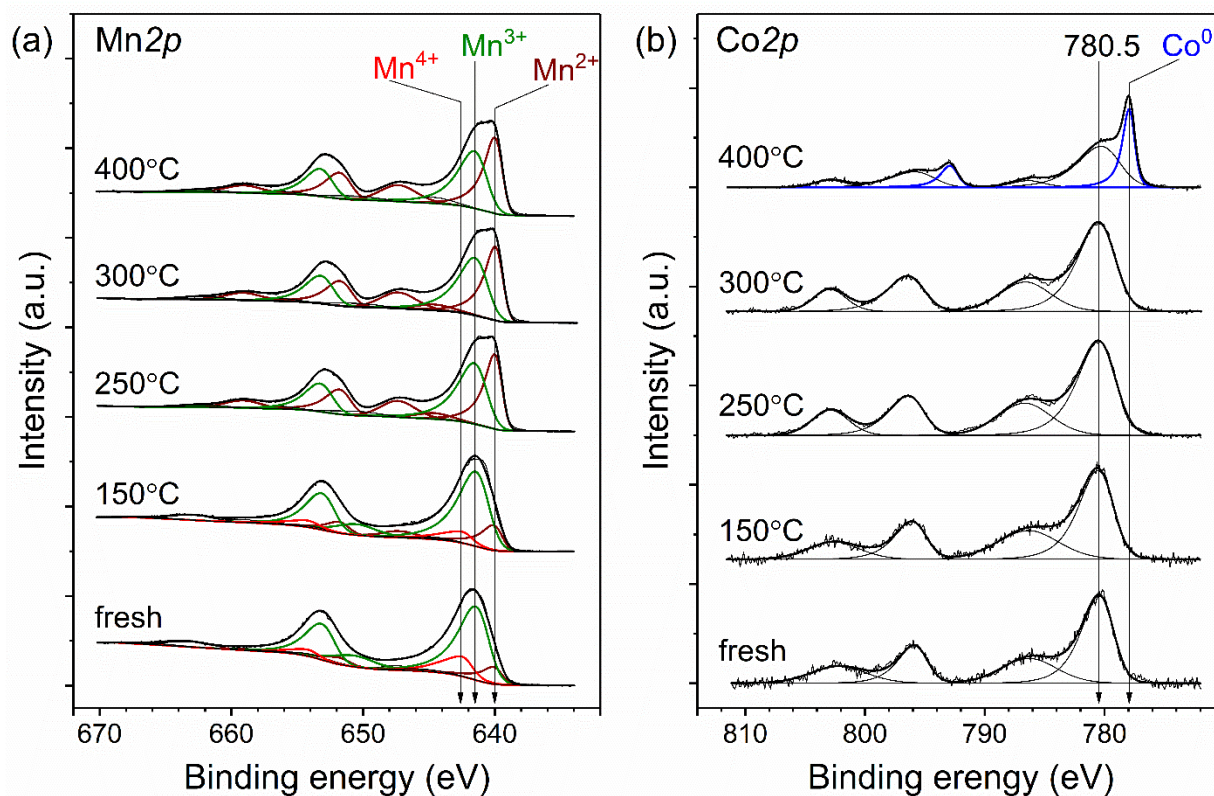


Figure 9. $Mn2p$ (a) and $Co2p$ (b) core-level spectra of the $Mn_{2.5}Co_{0.5}$ samples obtained before and after reductive treatment in hydrogen. The $Co2p$ spectra are normalized to the integrated intensity of the corresponding $Mn2p$ spectra.

During the reduction at temperatures up to 250 °C, the surface cobalt content gradually rises and the [Co]/[Mn] ratio increases from 0.128 to 0.200. In contrast, at 250-400 °C, the ratio decreases to 0.111. Apparently, cobalt ions diffuse into the bulk of the solid solution, despite the fact that, according to the *in situ* XRD and TPR results, the formation of (Mn,Co)O is observed in this temperature range. At 400 °C, the surface content of Co²⁺ begins to decrease and metallic cobalt appears, which obviously indicates the formation of Co⁰ clusters on the oxide surface.

The behavior of Mn is more complicated. During reduction at 250 °C, Mn⁴⁺ cations completely disappear. With the further heating, the fraction of Mn³⁺ decreases and the fraction of Mn²⁺ increases. The main peculiarity is that at 300-400 °C, the oxide surface contains about 50% of Mn³⁺, and its content does not change significantly. According to the XRD and TPR data, at 300-400 °C (Co,Mn)₃O₄ transforms to (Co,Mn)O. From the formal point of view, (Co, Mn)O contains cations in the 2+ oxidation state. Therefore, it can be assumed that fragments of the initial spinel including Mn³⁺ cations are still preserved on the surface. Perhaps, bulk reduction occurs, as it was observed previously for Co₃O₄ ⁶¹.

The study of Co-Mn oxide reducibility is strongly motivated by its application as a catalyst ^{23-27, 29-33}. Under reduction in hydrogen, cobalt oxide undergoes the following transformations: Co₃O₄

→ CoO → Co, while the reduction of manganese oxide leads to the transformation $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ ^{18, 19, 21, 60}. The temperature and pathway of the transformations depend on the preparation method, support, crystallite size, and composition of the reducing mixture ^{7, 21, 61}. The interaction of manganese and cobalt oxides leads to the formation of the mixed oxides, whose behavior is different from for the behavior of a mixture of simple oxides. Morales et al. ⁸ found that Co_3O_4 supported on TiO_2 catalysts was reduced to a mixture of CoO and Co at 425 °C. The introduction of Mn retards the reduction of supported Co_3O_4 particles. Latter authors ³² showed that, depending on the degree of interaction between manganese and cobalt in the oxide state, the reduction products exhibit different microstructural characteristics, which significantly affects their catalytic performance in the Fischer-Tropsch synthesis.

Our results are in line with the previous reports and indicate that introduction of manganese into cobalt oxide shifts the reduction temperature to a higher temperature region. At that, the growth of the Mn content results in an increase in temperature for both stages (Figure 8). The reducibility of oxides was studied by the TPR technique, which is a simple method to monitor the reduction process by using the amount of hydrogen that the sample adsorbs. It was demonstrated that TPR profiles of Mn-Co oxides change with a variation of the Mn:Co ratio ^{27, 33}. Qu et al. ²⁷ showed that

interaction between Co and Mn oxides for Mn:Co < 1 leads to a shift of TPR profiles to higher temperature region compared to simple oxides, indicating the worsening of the reducibility. For Mn:Co > 1, the TPR profiles exhibit new low temperature peaks. Wu et al.³³ found that the TPR curves of Mn-Co oxides are ascribed to the reductions of MnO₂/Mn₂O₃ to Mn₃O₄ and Co₃O₄ to CoO, and the broad reduction peak at >500 °C can be attributed to the reduction of Mn₃O₄ to MnO and CoO to Co. However, they found some effects, such as appearance of low- and high-temperature peaks, showing a strong synergistic effect between Co₃O₄ and MnO_x. It should be noted that during the synthesis, a mixture of different states is often formed (e.g. solid solutions based on cobalt and manganese oxide and simple oxides); therefore, there is a challenge to attribute the signal to the reduction of each compound. As a result, there is quite a lot of confusion in the literature with the interpretation of TPR results. Previously the mechanism of reduction of double oxides was investigated using a mixture of CoMn₂O₄ and MnCo₂O₄³⁴, and it was shown that the reduction process strongly differs from that observed for simple oxides Co₃O₄ and Mn₃O₄ in spite of similar TPR profiles. Reduction of CoMn₂O₄ and MnCo₂O₄ proceeds through the formation of intermediate compounds Mn_{0.6}Co_{0.4}O and Co_{0.6}Mn_{0.4}O to MnO and metallic Co. The results of the reported work show that the reduction of Co_{3-x}Mn_xO₄ occurs in two stages. The gradual

introduction of manganese cations into the structure of cobalt oxide slightly increases the temperature of the first reduction step $(\text{Mn,Co})_3\text{O}_4 \rightarrow (\text{Mn,Co})\text{O}$. In contrast, the influence of the addition of Mn onto the second stage is quite significant: the temperature of the transformation $(\text{Mn,Co})\text{O} \rightarrow \text{MnO} + \text{Co}$ shifts by ca. 500 °C. The presence of Mn and Co cations in the same spinel matrix significantly impairs oxide reducibility.

4. CONCLUSIONS

A series of $\text{Mn}_x\text{Co}_{3-x}$ samples with x varying from 0 to 2.9 was prepared by coprecipitation of cobalt and manganese nitrates with subsequent calcination at 600 °C in air. The initial oxides were characterized by XRD and XANES. The solubility limits of Mn and Co cations in the solid solution (spinel with a cubic or tetragonal structure) were determined. For x = 0.1-1.1, a solid solution is formed on the basis of the cubic spinel structure. For x = 1.3-1.7, there is a two-phase system consisting of cubic and tetragonal oxides, and for x = 1.9-2.9, a solid solution is formed on the basis of tetragonal spinel. The average oxidation state of manganese ions for the cubic oxide is higher (3.78+ - 3.86+) than that for the tetragonal modification (2.71+ - 3.08+).

The hydrogen reduction of Mn-Co oxides with the spinel structure was studied by *in situ* XRD, XPS, and TPR. It was found that the reduction of mixed oxides occurs in two stages. At the first

stage, the oxide $(\text{Mn,Co})_3\text{O}_4$ transforms to $(\text{Mn,Co})\text{O}$. At the second stage, the solid solutions $(\text{Mn,Co})\text{O}$ are reduced into metallic cobalt and MnO . The introduction of manganese into the structure of an oxide leads to an increase in the temperature of both stages, although to a different extent. Indeed, for the first stage, the structures of initial $(\text{Mn,Co})_3\text{O}_4$ and intermediate $(\text{Mn,Co})\text{O}$ oxides are similar, and conversion from one to another requires only a small displacement of cations. In contrast, the formation of metallic cobalt from $(\text{Mn,Co})\text{O}$ requires rearrangement of the entire structure, which makes the effect of manganese cations on the second stage of reduction much more significant. The combined use of *in situ* XRD and *pseudo in situ* XPS made it possible to detect the initial stages of the process: the reduction begins in the volume of the solid solution, then cobalt segregates and forms nanoparticles on the oxide surface, and only after a long time, there appears the crystalline phase of metallic cobalt.

It was shown that the gradual change in the chemical composition of a mixed oxide is a very promising approach to obtain detailed information about the route of the reduction. In its turn, the combined usage of *in situ* techniques directly determines the chemical state of cations under reductive conditions.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Supporting Information Available: XRD data (quantitative phase composition, lattice parameters, lattice volume, CSR and microstrains (ϵ_0) for the $\text{Mn}_x\text{Co}_{3-x}$ oxides *in situ* XRD results for $x=0.1$, 1.1, 1.9, 2.3, 2.7. This material is available free of charge via the Internet at <http://pubs.acs.org>

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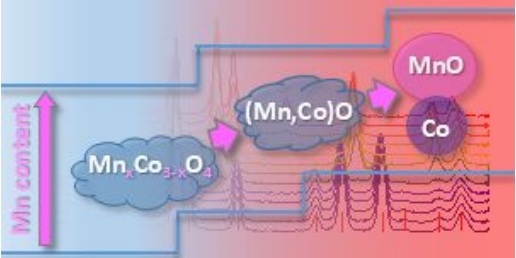
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The introduction of manganese into the structure of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ inhibits the two stages of oxide reducibility