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Ekaterina M. Sadovskaya, Dmitry D. Frolov, Vladimir B. Goncharov, Anna A. Fedorova, Igor V. Morozov, Alexander Yu. Klyushin, Alexander S. Vinogradov, Ekaterina A. Smal*, Vladislav A. Sadykov

Mixed spinel-type Ni-Co-Mn oxides: synthesis, structure and catalytic properties

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Abstract: Mixed spinel-type oxides $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$, $\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ prepared by thermal decomposition of nitrates have been studied in ethanol steam reforming reaction. $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ demonstrated the highest activity among the oxides tested. Specificity of the cation distribution in the samples and their oxygen mobility have been studied by X-ray absorption spectroscopy and oxygen isotope heteroexchange, respectively. Doping of mixed cobalt-manganese spinel with Ni results in Mn redistribution between 3+ and 4+ oxidation states, thus increasing oxygen diffusion coefficient and the catalytic activity.

Keywords: Spinel, Ethanol steam reforming, Oxygen isotope exchange, X-ray absorption spectroscopy.

1 Introduction

Ethanol steam reforming (ESR) process is now of a great interest for hydrogen production. Hydrogen is considered

to be the most efficient fuel in terms of the highest energy/mass ratio among hydrocarbon fuels. Also, hydrogen fuel cells are environmental friendly since they do not emit CO_2 into atmosphere. Catalysts with different types of both active components and supports were studied in ESR reaction. Noble (Rh [1], Ru, Pt, Pd [2], Ir [3]) and non-noble (Co [4], Ni [5]) metals were the most used active components. Simple (ZnO [6], CuO [7]) and basic (ZnO [8], La_2O_3 , Y_2O_3 [4, 9]) oxides, perovskites (LaNiO_3 [10]), oxide with fluorite structure (CeO_2 [3, 11]), $\gamma\text{-Al}_2\text{O}_3$ [2, 12], SiO_2 [5, 6] were used as supports. Spinel-based catalysts including monometallic Co_3O_4 [13], two-component systems (NiM_2O_4 , $\text{M}=\text{Al}$, Fe, Mn [14]; MAl_2O_4 , $\text{M}=\text{Zn}$, Ni, Cu [15]; ZnM_2O_4 , $\text{M}=\text{Al}$, Co, Fe [16]) and some other spinel-type systems with spinel being the main phase (Mg-Ni-Al-O, Zn-Co-Ni-Al-O, Cu-Ni-Zn-Al-O, *etc.*) [17–20] were also studied. Such studies aim at replacing currently used noble and rare-earth metals containing catalysts by the cheaper and accessible ones. All the works mentioned note that at contact time ~ 0.1 s spinels provide 100% ethanol conversion at temperatures exceeding 600°C . In the present paper mixed spinel-type oxides $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$, $\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ were studied by X-ray absorption spectroscopy (XAS) and oxygen isotope heteroexchange, their catalytic performance was investigated in ESR reaction.

2 Experimental

2.1 Synthesis

$\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$, $\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ mixed oxides were prepared by the thermal decomposition of mixed nitrate salts by the following route: 1) heating from room temperature to 120°C in 1 hour, 2) annealing at 120°C for 1 hour, 3) heating from 120°C to 320°C in 1 hour, 4) annealing at 320°C for 1 hour, 5) heating from 320°C to 720°C in 2 hours, and 6) annealing at 720°C for 1 hour. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salts

*Corresponding author Ekaterina A. Smal, Boreskov Institute of Catalysis, 630090, Novosibirsk, Russia, E-mail: alageizia@mail.ru
 Ekaterina M. Sadovskaya, Vladimir B. Goncharov, Vladislav A. Sadykov, Boreskov Institute of Catalysis, 630090, Novosibirsk, Russia
 Ekaterina M. Sadovskaya, Vladislav A. Sadykov, Novosibirsk State University, 630090, Novosibirsk, Russia
 Dmitry D. Frolov, Anna A. Fedorova, Igor V. Morozov, Lomonosov Moscow State University, Department of Chemistry, 119991, Moscow, Russia
 Alexander Yu. Klyushin, Alexander S. Vinogradov, V.A. Fock Institute of Physics, St. Petersburg State University, 198504, St. Petersburg, Russia
 Alexander Yu. Klyushin, Division Energy Material, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany

were used for synthesis, the purity of all reagents was not lower than 99 at.%. The samples prepared were fine black powders.

2.2 Characterization

The crystalline structure of the samples (both as-prepared and after temperature-programmed reduction by ethanol) was studied by X-ray diffraction (DRON-3 diffractometer, CuK α or CoK α radiation). Surface area measurements were performed by using BET method with N₂ adsorption (Chemisorb 2750, Micromeritics). XAS measurements were performed at the Russian-German beamline [21] operated at the electron storage ring HZB/BESSY II (Berlin, Germany). The samples for measurement (both catalysts powders and reference compounds) were prepared by rubbing onto the scratched clean surface of copper plates of size 5 × 5 mm². The samples were placed at an angle of ~45° with respect to the incident beam of monochromatic radiation.

The NEXAFS (Near-Edge X-ray Absorption Fine Structure) spectra were obtained by recording the total electron yield (TEY) of the X-ray photoemission in the mode of drain current measurement from the sample by varying the energy of incident photons. The monochromator energy resolutions in the range of the Ni 2p absorption edge (photon energy $h\nu \sim 850$ eV), the Co 2p absorption edge ($h\nu \sim 770$ eV) and the Mn 2p absorption edge ($h\nu \sim 640$ eV) were equal to 280 meV, 250 meV and 170 meV, respectively. The X-ray absorption spectra were normalized with respect to the incident photon flux, which was monitored by recording the TEY from the clean surface of a gold mesh mounted on the manipulator holder. The $h\nu$ in the range of the fine structure of the transition metal X-ray absorption spectra was calibrated against the energy positions of the first narrow peak in the F 1s X-ray absorption spectrum of K₂TiF₆ (683.9 eV) [22].

Several samples of each type were prepared, the spectra recorded several times from different points of each sample showed a good reproducibility. Sample charging effects were not observed during the absorption measurements. All X-ray absorption spectra were measured under a ultrahigh vacuum of 2×10^{-10} mbar in the analytic chamber.

2.3 Oxygen isotope exchange

After reaching equilibration at 700°C with the 1%¹⁶O₂ + Ar flow in the reactor (quartz tube, ID = 3 mm, L = 120 mm), the gas mixture was switched to the one containing ¹⁸O₂. Both the gas flow rate (50 ml/min) and catalyst loading (0.03 g) were kept constant in all the experiments. The fraction of ¹⁸O isotope in oxygen was 96%. The transient changes in the gas isotopic composition (¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂ concentrations) were continuously monitored by VG Sensorlab 200D mass spectrometer. Atomic fraction of ¹⁸O in gaseous oxygen was calculated based on the following mass-spectrometric data:

$$\alpha_g = \frac{2 \times I_{36} + I_{34}}{2 \times (I_{36} + I_{34} + I_{32})}$$

where I_{32} , I_{34} and I_{36} are parent peaks at m/e 32, 34, 36.

2.4 Ethanol steam reforming

Catalysts were studied in three different reactions: reduction by ethanol, reoxidation by water in the temperature-programmed modes and ESR in the steady-state conditions. Both temperature-programmed and steady-state experiments were carried out in a flow quartz reactor (contact time 36 ms) using a kinetic installation with on-line analysis of the exit stream by IR absorbance, electrochemical and polarographic gas sensors for different components [23].

Samples ($m = 0.3$ g) were pre-treated in oxygen at 500°C, after that cooled in He flow and reduced by 1% C₂H₅OH in He flow in the temperature-programmed reduction (TPR) mode (flow rate 10 l/h and temperature ramp from 25°C to 880°C at 10°C/min followed by a plateau at 880°C for 40 min) and then rapidly cooled in pure He. Reduced samples were reoxidized by water (1% H₂O in He, flow rate 10 l/h) using the same temperature program as in the ethanol TPR-mode. Reoxidized samples were then studied in ESR reaction with reaction feed containing 0.5% C₂H₅OH + 2% H₂O in He flow (flow rate 20 l/h). Samples were heated up to 800°C and kept at this temperature until the steady-state performance in the reaction mixture had been reached. Then the temperature was decreased by 50-100°C steps by keeping sample at each temperature until a stationary conversion had been achieved.

3 Results and discussion

3.1 XRD study

BET surface area of samples was found to be relatively small (3–8 m²/g).

Figure 1a and 1b shows XRD patterns of as-prepared and reduced $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ catalysts, respectively. All initial catalysts consisted of single-phase spinel without any admixtures. Reduced samples changed their structure. $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ catalyst was reduced to metallic Co and mixed rocksalt-type oxide (Mn,Co)O. Whereas, in the case of $\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ samples, it is hard to distinguish the reduction products due to their high structure similarity; the first group of similar products contained metallic Ni and Co, and the second group contained mixed rocksalt-type oxides (Mn,Co,Ni)O. According to literature, only some spinels (i.e. MgAl_2O_4 , ZnAl_2O_4 [16]) are stable in the reaction conditions of ethanol steam reforming. Other spinels containing transition metals (Fe, Co, Ni, Cu) are usually reduced into the mixture of metals and oxides [14–16]. Metallic Mn is not observed in Mn-containing spinels, since Mn oxides can be reduced only to MnO in such conditions.

3.2 X-ray absorption spectroscopy

The common spinel AB_2O_4 has two types of cation sites A and B: with tetrahedral and octahedral coordination by oxygen, respectively. If the tetrahedral sites are occupied only by A-type cations the spinel structure is referred to as a normal one, and if the tetrahedral sites are occupied

only by B-type cations the spinel structure is inverted one. Of course, there are many spinels with mixed (both A and B types) filling of tetrahedral sites, they are called partially inverted.

To interpret XAS spectra some reference samples with known structure were studied. Co_3O_4 ($\text{Co}^{2+}[\text{Co}^{3+}_2]\text{O}_4$), CoCr_2O_4 ($\text{Co}^{2+}[\text{Cr}^{3+}_2]\text{O}_4$), NiO, Mn_2O_3 , MnO_2 were chosen as such references. Square brackets represent cations occupying octahedral sites. The latter two samples contain Mn only in octahedral sites.

All spectra of Co- and Mn-containing samples are presented in Figure 2. The main absorption structures A and B in the Co 2p_{3/2} (Figure 2A) spectra can be described in the framework of atomic multiplet calculations with the inclusion of cubic crystal field splitting for 2p⁶3dⁿ → 2p⁵3dⁿ⁺¹ atomic excitations [24,25]. In Figure 2B Mn 2p_{3/2} spectra of the spinel samples are compared with manganese oxides references; two main absorption structures B and E in the Mn 2p_{3/2} spectrum of MnO_2 (Mn^{4+}) can be assigned as a core electron transition to unoccupied antibonding molecular t_{2g} and e_g orbitals of octahedral quasimolecule MnO_6^{8-} [26]. The presence of an additional d-electron in final state of Mn_2O_3 (Mn^{3+}) has the effect of lifting the orbital and electronic degeneracies and lowering the overall energy, the so called Jahn–Teller effect [27], which leads to appearance of the A–D bands in the Mn 2p_{3/2} spectrum of Mn_2O_3 instead of two bands in MnO_2 . The reference spectra can be used as fingerprints to determine the oxidation state of Mn in spinel samples. According to these data, doping of $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ spinel by Ni results in substitution of Co^{3+} in octahedral sites by Ni^{2+} , leading to the transformation of part of Mn^{3+} to Mn^{4+} to keep electroneutrality.

Ni spectra of catalysts and reference compounds are identical, therefore they are not shown. The spectra of Ni-Co-Mn-O samples were approximated by the linear

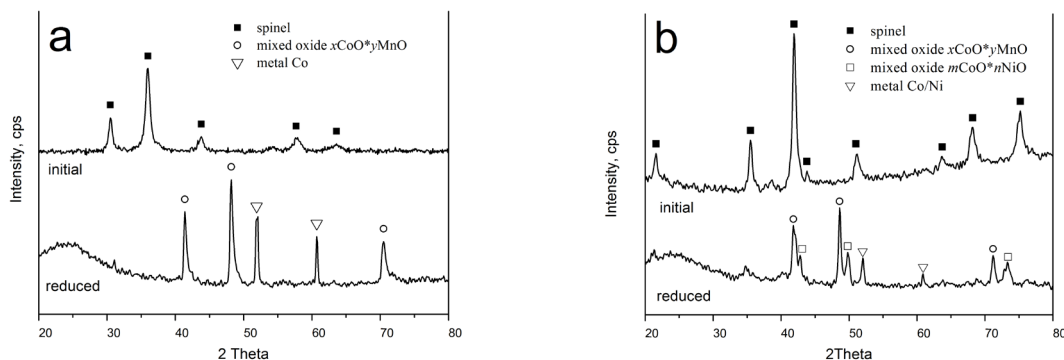


Figure 1. XRD patterns of initial and reduced samples: *a* – $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$, *b* – $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$. Pattern of initial $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ sample was obtained by using CuK α radiation, all others – by using CoK α radiation.

combination of the reference spectra. The results of the revealed cation distribution are presented in Table 1.

Table 1. Revealed cation distribution in Ni-Co-Mn-O spinel-type oxides from XAS experiments

Oxide	Cation distribution
Co_3O_4	$[\text{Co}^{2+}]_T [\text{Co}_2^{3+}]_O \text{O}_4$
$\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$	$\text{Co}^{2+} [\text{Co}_{0.8}^{3+}\text{Mn}_{1.2}^{3+}] \text{O}_4$
$\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$	$\text{Co}^{2+} [\text{Co}_{0.33}^{3+}\text{Ni}_{0.33}^{2+}\text{Mn}_{1.33}^{3+}\text{Mn}_{0.33}^{4+}] \text{O}_4$
$\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$	$\text{Co}^{2+} [\text{Co}_{0.2}^{3+}\text{Ni}_{0.6}^{2+}\text{Mn}_{0.6}^{3+}\text{Mn}_{0.6}^{4+}] \text{O}_4$

3.3 Oxygen isotope exchange

The time dependencies of ^{18}O isotope fractions in O_2 (α_g) obtained after the stepwise $^{16}\text{O}_2$ substitution by $^{18}\text{O}_2$ in the feed gas are shown in Figure 3a. In the case of the Co_3O_4 sample the atomic fraction of ^{18}O registered at the reactor outlet reaches the value corresponding to the isotope fraction at the reactor inlet almost immediately. So in this case the amount of oxygen of oxide involved into the isotopic heteroexchange with gaseous oxygen is small due to a low rate of oxygen diffusion in the bulk of particles [28]. For mixed oxides the fraction of ^{18}O in the outlet

mixture is much smaller than in the inlet suggesting quite intense isotopic heteroexchange and much higher amount

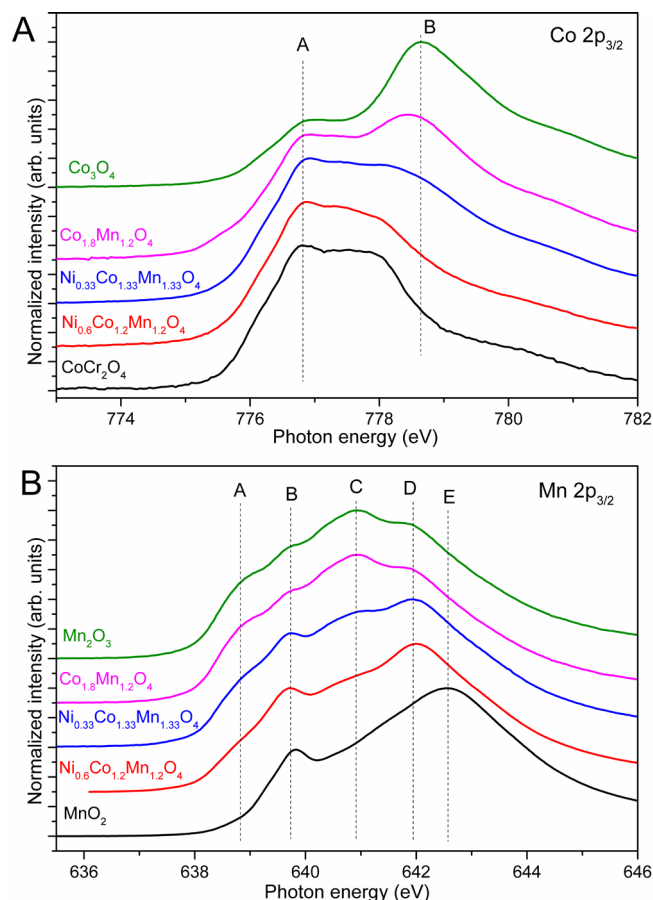


Figure 2. (A) Co and (B) Mn $2p_{3/2}$ XAS spectra of references and samples investigated.

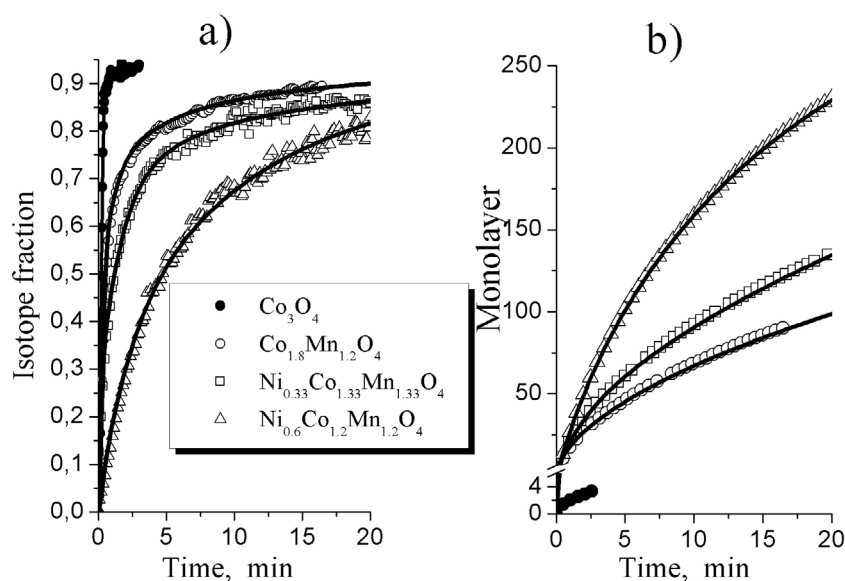


Figure 3. The oxygen isotope exchange on Co_3O_4 , $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$, $\text{Ni}_{0.33}\text{Co}_{1.33}\text{Mn}_{1.33}\text{O}_4$, $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ at 700°C : a) time dependencies of ^{18}O isotope fractions in O_2 , b) the amount of exchanged oxide oxygen depending on time. Dots – experiment, lines – numerical modeling.

of bulk oxygen of oxide particles involved in this process. The isotope fraction gradually approached its value in the inlet stream as the isotopic substitution of oxide oxygen occurred. The amount of substituted oxygen of oxide as a function of time of exchange can be calculated by integrating the function $\alpha_g(t)$:

$$N_o(t) = 2 \frac{U \times C_{O_2}}{g \times S \times L \times 100\%} \int_0^t (0.96 - \alpha_g) dt$$

Here, N_o is the number of monolayers of substituted oxide oxygen, U – the molar flow rate (mol/min), C_{O_2} – oxygen concentration in the stream, g – sample weight, S – surface area, L – monolayer coverage (assumed to be equal to 0.17×10^{-4} mol/m², that corresponds to 1×10^{19} at/m²).

Thus obtained dependencies $N_o(t)$ are presented in Figure 3b. These data show that intensity of oxygen isotopic exchange increases in the series: $Co_3O_4 < Co_{1.8}Mn_{1.2}O_4 < Ni_{0.33}Co_{1.33}Mn_{1.33}O_4 < Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$.

The amount of oxygen which can be exchanged in Co_3O_4 agrees with earlier obtained estimations of the weakly bound oxygen species removed from this oxide by temperature-programmed desorption [25]. It is explained by the oxidation of the oxide surface layers under contact with air up to Co_2O_3 stoichiometry, while the bulk of particles may remain Co_3O_4 composition with a low oxygen mobility.

Based on the numerical analysis of isotope exchange data, the oxygen diffusion coefficients in the bulk of samples were estimated. The kinetics of isotope exchange between the gas-phase oxygen and the oxide oxygen is described by the following equations:

$$C_{O_2} \left(\frac{\partial \alpha_g}{\partial t} + \frac{1}{\tau} \frac{\partial \alpha_g}{\partial \xi} \right) = -bR(\alpha_g - \alpha_s) \quad (1)$$

$$\frac{\partial \alpha_s}{\partial t} = R(\alpha_g - \alpha_s) - \frac{N_{bulk}}{N_s} \frac{D}{h^2} \frac{\partial \alpha_{bulk}}{\partial \eta} \Big|_{\eta=0} \quad (2)$$

$$\frac{\partial \alpha_{o,bulk}}{\partial t} = \frac{D}{h^2} \frac{\partial^2 \alpha_{o,bulk}}{\partial \eta^2} \quad (3)$$

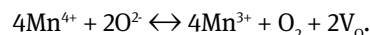
Here, α_g , α_s , α_{bulk} – molar fractions of ^{18}O isotope in the gas phase, on the sample surface and in the sample bulk, respectively; R – exchange rate; τ – contact time (s); b – the ratio of the surface active centers (N_s) to the number of oxygen atoms in the sample bulk (N_{bulk}): $b = N_s/N_{bulk}$; h – characteristic size of sample particles; $\frac{D}{\Delta h^2}$ – normalized diffusion coefficient (s⁻¹) (where $\Delta h = h \frac{N_s}{N_{bulk}}$ is one oxygen monolayer depth and D – bulk oxygen self-diffusion coefficient, cm²/s); t – time; ξ – dimensionless length of reactor; η – dimensionless depth of the oxygen layer in oxide particles.

The calculated diffusion coefficients obtained by fitting the calculated dependency $\alpha_g(t)$ to the experimental data are given in Table 2.

Table 2. Diffusion coefficients at 700°C

Sample	D, cm ² /s
$Co_{1.8}Mn_{1.2}O_4$	0.8×10^{-12}
$Ni_{0.33}Co_{1.33}Mn_{1.33}O_4$	1.5×10^{-12}
$Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$	10×10^{-12}

The change of the lattice oxygen mobility can be explained by taking variation of the samples structure into account. Thus, a part of Co^{3+} is substituted by Mn^{3+} cation in $Co_{1.8}Mn_{1.2}O_4$ oxide as compared with Co_3O_4 . According to XRD data, this substitution does not distort the sample structure, but Mn^{3+} incorporation into the lattice weakens the “rigid” Co_3O_4 structure. Introducing stable Ni^{2+} cations and occupation of a part of octahedral sites leads to such effect that a part of Mn cations change their oxidation state from 3+ to 4+ to preserve a total charge of the cation sublattice. Such variation leads to formation of redox cations ($Co^{2+}-Mn^{4+}$) pairs, within which the electron transfer is possible. Cations with a higher oxidation states might promote the redox reactions involving oxygen that can be presented by the following quasichemical equation:



3.4 Catalytic tests

Samples $Co_{1.8}Mn_{1.2}O_4$ and $Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$ were studied in the reaction of ethanol steam reforming (vide supra). H_2 and carbon oxides were the main products during TPR by ethanol, corresponding curves are presented in Figure 4. Activity of $Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$ is higher than that of $Co_{1.8}Mn_{1.2}O_4$ sample. This is consistent with the literature data, which confirm that catalysts containing both Ni and Co are more active and provide a higher hydrogen yield than only Co-containing catalysts [29, 30].

Ratios of the integral amount of oxygen and hydrogen atoms in products of TPR are 1.2:6, и 1.3:6 for $Co_{1.8}Mn_{1.2}O_4$ and $Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$, respectively. In both cases these ratios are higher than O/H ratio in the molecule of ethanol (1:6) suggesting that oxygen of mixed oxides takes part in carbon oxides formation. The estimated reduction degree in this experiment is 4.5% for $Co_{1.8}Mn_{1.2}O_4$ and 6% for $Ni_{0.6}Co_{1.2}Mn_{1.2}O_4$.

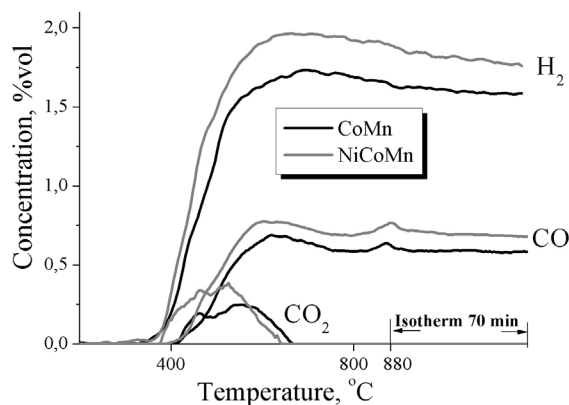


Figure 4. EtOH TPR curves for $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ samples

At the same time, the ratios of carbon and hydrogen atoms in products (about 0.6:3 in both cases) are lower than in the molecule of ethanol (1:3). It means that carbon and/or carbon-containing compounds were deposited on the samples surface. During subsequent temperature-programmed reoxidation by water, carbon deposits were oxidized by water forming carbon oxides and hydrogen as products (Figure 5), while surface reoxidation occurs simultaneously. This reoxidation of the catalyst is also confirmed by the balance ratio of hydrogen and carbon oxides evolved during reaction.

Oxidation by water occurs more actively for $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ sample, correlating with a higher rate of EtOH TPR. This sample also shows a higher activity in stationary conditions of ethanol steam reforming at lower temperatures (Figure 6).

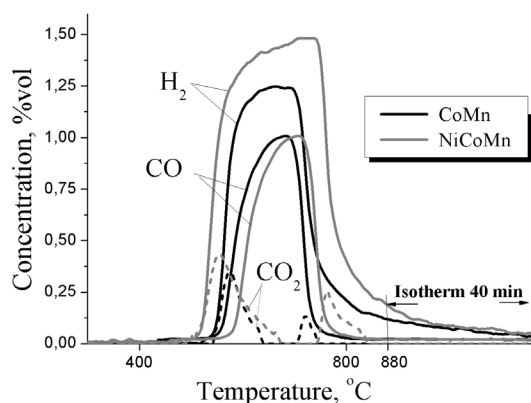


Figure 5. Temperature-programmed oxidation by water of $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ samples

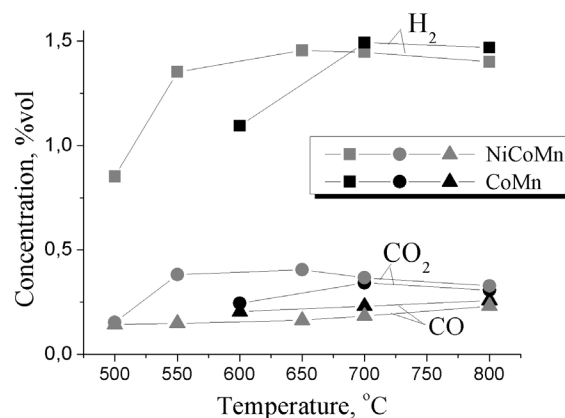


Figure 6. ESR reaction in steady-state mode on $\text{Co}_{1.8}\text{Mn}_{1.2}\text{O}_4$ and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$

Hence, this study demonstrates correlation between the oxygen mobility of spinel samples, their redox properties and activity in the ESR reaction, which is determined by the spinel chemical composition and cations distribution.

4 Conclusions

Mixed spinel-type Ni-Co-Mn oxides have been prepared by thermal decomposition of metal nitrates. The initial oxides contained single-phase spinel without any admixtures; while reduced samples consisted of metallic Ni and/or Co and rocksalt-type oxide. According to XAS data the modification by Ni resulted in substitution of Co^{3+} in octahedral sites by Ni^{2+} cations, which leads to a partial transformation of Mn^{3+} to Mn^{4+} to preserve the total charge of cation sublattice. The oxygen diffusion coefficients in the bulk of samples have been evaluated and $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ exhibited the highest value equal to $10 \times 10^{-12} \text{ cm}^2/\text{s}$ at 700°C . This can be explained by Mn redistribution between 3+ and 4+ oxidation states which led to formation of redox cations ($\text{Co}^{2+}\text{-Mn}^{4+}$) pairs, within which the electron transfer was possible. Formation of cations with a high oxidation degree might have promoted redox reactions involving oxygen. Among the samples tested, $\text{Ni}_{0.6}\text{Co}_{1.2}\text{Mn}_{1.2}\text{O}_4$ demonstrated the highest activity in ethanol steam reforming.

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