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# Oxidation of Carbon Monoxide over MLaO<sub>x</sub> Perovskites Supported on Mesoporous Zirconia

Nikolai A. Davshan,<sup>[a]</sup> Alexander L. Kustov,<sup>[a]</sup> Olga P. Tkachenko,<sup>[a]</sup> Leonid M. Kustov,<sup>\*[a, b]</sup> and Chang Hwan Kim<sup>[c]</sup>

The oxidation of CO was studied on a series of  $MLaO_3$  perovskites (M=Co, Fe, Ni) supported on mesoporous zirconia that are synthesized by using a glycine-mediated method and characterized by using X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and diffuse reflectance infrared Fourier transform spectroscopy. The activity of the catalysts in the CO oxidation reaction follows the order Co > Ni > Fe.

## Introduction

Controlling exhaust gas emissions is a problem of utmost concern.<sup>[1]</sup> Mixed metal oxides with a composition ABO<sub>3</sub> known as perovskites<sup>[2,3]</sup> demonstrate high thermal stability and enhanced catalytic activity in CO and hydrocarbon oxidation. The perovskite-type materials are less expensive than the supported noble metals. The major drawback of perovskite catalysts is the low specific surface area (a few m<sup>2</sup>g<sup>-1</sup>). The materials can be significantly improved by supporting the perovskites on porous carriers with a developed surface area.<sup>[4]</sup> Mesoporous zirconia is of special interest as a durable carrier. The porous structure of  $ZrO_2$  helps in the formation and stabilization of nanoparticles of the active component by preventing their migration, coalescence, and sintering in the course of high-temperature processes occurring in catalytic processes.

The ZrO<sub>2</sub>-supported perovskites were synthesized and studied herein as CO oxidation catalysts. Pechini supported perovskites LaBO<sub>3</sub> (B=Mn, Fe, Co, Ni, Cu) on a cordierite honeycomb support<sup>[5]</sup> and succeeded in the preparation of supported catalysts that are resistant to high temperatures<sup>[6]</sup> Cordierite-supported lanthanum manganite and cobaltite are shown to be quite active in the oxidation reactions, especially if supported on a secondary sublayer (Ln<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and LaBO<sub>3</sub>).

[a]	N. A. Davshan, A. L. Kustov, O. P. Tkachenko, Prof. L. M. Kustov N.D. Zelinsky Institute of Organic Chemistry
	Russian Academy of Sciences
	47 Leninsky prospect, Moscow 119991 (Russian Federation) Fax: (+ 7)4991372935
	E-mail: LMK@ioc.ac.ru
[b]	Prof. L. M. Kustov
	Chemistry Department
	Moscow State University
	1 Leninskie Gory, Bldg 3, Moscow119992 (Russian Federation)
[c]	C. H. Kim
	General Motors Global Research and Development
	Chemical Sciences & Materials Systems Laboratory
	30500 Mound Rd., Warren, MI 48090 (USA)
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The use of mixed perovskite membranes for simultaneous in situ oxygen separation and catalytic oxidation has been reported.<sup>[7]</sup> Ca and Sr-substituted lanthanum ferrite perovskites (La<sub>1-x</sub>A<sub>x</sub>FeO<sub>3</sub>, A=Ca, Sr and x=0.1–0.2) were prepared by means of a conventional method using citric acid. The oxidation processes over these catalytic membranes were performed at 1000–1333 K, and the catalysts demonstrated stable performance for several days on stream.

The perovskite-type LaSrCoO<sub>4</sub> mixed oxides were prepared by using the gelatin, polyglycol gel, and polyacrylamide gel methods, and these oxides were used for CO and  $C_3H_8$  oxidation.<sup>[8]</sup> The catalytic activity of LaSrCoO<sub>4</sub> prepared by using the polyacrylamide gel method was the highest, which was explained in terms of the higher mobility of oxygen vacancies and lattice oxygen, smaller particle size, and larger BET surface areas.

LaMn<sub>1-x</sub>Cu<sub>x</sub>O<sub>3±δ</sub> perovskite oxides (x=0-1) were prepared by using the Pechini and sol–gel methods.<sup>[9]</sup> The catalysts demonstrated excellent catalytic activity in the oxidation of methane and CO. The Pechini samples were more homogeneous and contained smaller particles (higher specific surface area). In CO oxidation, the oxides with x=0.2 and 0.4 were the most active. The Pechini samples demonstrated higher activity and stability than the sol–gel samples.

The perovskite-type catalysts with LaCoO<sub>3</sub> and La<sub>0.9</sub>Ba<sub>0.1</sub>CoO<sub>3</sub> compositions have been prepared by using the sol-gel method, and their catalytic activity was studied in CO oxidation.<sup>[10]</sup> The La<sub>0.8</sub>Ba<sub>0.1</sub>CoO<sub>3</sub> catalyst demonstrated enhanced catalytic activity as compared with the LaCoO<sub>3</sub> catalyst. Barium substitution appears to be responsible for the low-temperature activity of the catalyst by affecting the redox and oxygen desorption properties.

Modified perovskite-type oxides synthesized through coprecipitation and a conventional citrate method<sup>[11]</sup> (LaCoO<sub>3</sub>, La-Co<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub>, La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub>, and La<sub>0.8</sub>M<sub>0.2</sub>FeO<sub>3</sub>, M = Ce and Sr) demonstrated high catalytic activity in the low-temperature CO oxidation, and the samples manifested good stability up to 600 °C. La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub> showed CO conversions close to 100% at 355 °C. Of the other four synthesized perovskite formulations, the LaCoO<sub>3</sub> sample was the best performer in the whole range of CO conversions.

The perovskite-type catalysts La<sub>0.7</sub>Sr<sub>0.3</sub>Cr<sub>1-x</sub>Ru<sub>x</sub>O<sub>3</sub> (0.025 < x < 0.100) were synthesized by annealing a mixture of metal oxides and carbonates up to 1000 °C in air.<sup>[12]</sup> The CO oxidation activity increases with the increase in the degree of substitution (*x*). The concentration of Ru<sup>4+</sup> on the surface and its stability are the determining factors for the CO oxidation activity. The important conclusions drawn herein are that Ru perovskites have high thermal stability and high CO oxidation activity.

The unsupported and supported LaRuO<sub>3</sub>-type lanthanum ruthenate perovskites<sup>[13]</sup> were synthesized through freeze drying, in situ synthesis, coprecipitation, and deposition precipitation. These innovative synthesis methods lead to the formation of LaRuO<sub>3</sub> with improved catalytic properties. LaRuO<sub>3</sub> also demonstrates a reasonably high thermal stability and can be a potential candidate for many catalytic reactions even at elevated temperatures.

The ZrO<sub>2</sub>-supported La and Mn oxide catalysts with different La and Mn loadings (0.7–16 wt % as LaMnO<sub>3</sub>) were prepared<sup>[14]</sup> through the impregnation of tetragonal ZrO<sub>2</sub> with La and Mn citrates. The presence of a perovskite-like structure is necessary for the development of highly active sites for CO oxidation at 350–800 K.

The perovskite-type oxides La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x=0–0.1) were prepared and evaluated in the selective CO oxidation in hydrogen.<sup>[15]</sup> The citrate synthesis methodology favored the formation of perovskites with a low specific surface area (<14 m<sup>2</sup>g<sup>-1</sup>). The catalytic test results in the CO oxidation reaction revealed a 100% CO conversion at 200 °C. LaCoO<sub>3</sub> and La<sub>0.95</sub>Ce<sub>0.05</sub>CoO<sub>3</sub> catalysts demonstrated good stability.

Ba(Ce,Pd)O<sub>3</sub> perovskite demonstrated an unusual behavior<sup>[16]</sup> in CO oxidation by oxygen, in spite of the low surface area. If O<sub>2</sub> is present in excess, the kinetics show CO inhibition consistent with a Langmuir–Hinshelwood mechanism in which both reactants compete for the same adsorption sites. The Arrhenius activation energy for this reaction is surprisingly low, 7.8  $\pm$ 0.3 kcal mol<sup>-1</sup>. This low value is due to the weak adsorption of CO on Pd<sup>2+</sup> ionic sites located at the catalyst surface. If the concentration of O<sub>2</sub> is limited, the reaction orders for both CO and O<sub>2</sub> show a strong dependence on the  $P_{CO}/P_{O2}$  ratio. The catalytic activity of Pd-substituted BaCeO<sub>3</sub> is attributed to the increased bulk oxygen mobility in the presence of square planar Pd<sup>2+</sup> ions that are located at the perovskite B sites, each adjacent to an oxygen vacancy.

Jin et al. generalized the results of long-term efforts aimed at research and development of industrial oxide catalysts for oxidation processes.<sup>[17]</sup> The bonding strength of the surface oxygen determined from the surface atomic structure appears to be the most important factor. The existing approaches to the synthesis of mixed oxide systems such as perovskites with good stability in the high-temperature processes are analyzed.

Thus, the number of papers devoted to perovskites supported on appropriate mesoporous matrices is limited, though diverse mesoporous materials, such as silicates (MCM-41, SBA-15, etc.) or layered double hydroxides (clays and hydrotalcites), or hierarchical zeolites deserve attention as carriers for the oxidation-type catalysts.<sup>[18,19]</sup>

The goal of this article was to prepare, characterize, and test in CO oxidation a series of  $MLaO_3$  perovskites (M=Co, Fe, Ni) supported on mesoporous zirconia acting as a robust and durable carrier.

## **Results and Discussion**

#### Characterization of the supported perovskites

#### SEM and surface area

The SEM data reveal that the perovskites LaMO<sub>3</sub> (M=Co, Ni, Fe) supported on mesoporous zirconia are amorphous materials (see the Supporting Information). The BET surface areas of the three catalysts measured by using nitrogen adsorption differ insignificantly: 155, 143, and  $135 \text{ m}^2 \text{g}^{-1}$  for LaCoO<sub>3</sub>, LaNiO<sub>3</sub>, and LaFeO<sub>3</sub>. The dispersion of the perovskites supported on mesoporous zirconia is high and uniform with the size of nanoparticles below 2–3 nm, as confirmed by the absence of any reflections in the XRD patterns (region of coherent scattering).

#### Diffuse reflectance infrared Fourier transform spectroscopy

The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the three samples prepared by supporting  $LaCoO_{xr}$   $LaFeO_{xr}$  and  $LaNiO_x$  on mesoporous zirconia and calcined at 600 °C are shown in Figure 1. The hydroxyl groups are characterized by the stretching frequencies of 3673, 3678, and 3680 cm<sup>-1</sup> attributed to the vibrations of terminal Zr–OH.<sup>[26]</sup> Notably, no distinct bands attributable to the supported perovskites encapsulated in the mesopores of ZrO<sub>2</sub> are observed in the spectra.

The presence of Lewis acid sites on the surface of these catalysts, as well as their relative strengths, can be studied by using the spectra of adsorbed CO and  $CD_3CN$ . The high-frequency shifts for CO and  $CD_3CN$  relative to the gas-phase frequencies of these molecules are observed owing to the inter-



Figure 1. IR spectra of OH groups for the  $LaCoO_x/ZrO_2$ ,  $LaFeO_x/ZrO_2$ , and  $LaNiO_x/ZrO_2$  samples.

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actions with metal cations (Lewis acid sites). The spectra of the samples after the adsorption of CO and  $CD_3CN$  are shown in Figures 2 and 3, respectively.



Figure 2. IR spectra of CO adsorbed on the LaCoO\_x/ZrO\_2, LaFeO\_x/ZrO\_2, and LaNiO\_x/ZrO\_2 samples.



Figure 3. IR spectra of CD<sub>3</sub>CN adsorbed on the LaCoO<sub>x</sub>/ZrO<sub>2</sub>, LaFeO<sub>x</sub>/ZrO<sub>2</sub>, and LaNiO<sub>x</sub>/ZrO<sub>2</sub> samples.

The spectrum of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample demonstrates absorption bands at 2137 cm<sup>-1</sup> (main band) and low-intensity bands at 2058 and 1981 cm<sup>-1</sup> after CO adsorption (Figure 2). The band at 2137 cm<sup>-1</sup> attributed to its low frequency most likely belongs to CO complexes with low-coordinated Co ions—Co<sup>2+</sup> in agreement with the literature data.<sup>[27]</sup> The presence of two oxidation states of Co is in good agreement with the literature data on the loss of a part of mobile oxygen by perovskites upon high-temperature annealing,<sup>[28]</sup> owing to the LaCo<sup>+3</sup>O<sub>3</sub>→LaCo<sup>+2</sup>O<sub>2.5</sub>+<sup>1</sup>/<sub>2</sub>O<sub>2</sub> transition. The doublet bands at 2058 and 1981 cm<sup>-1</sup> may be assigned to the di- and tricarbonyl species Co(CO)<sub>2</sub> and Co(CO)<sub>3</sub> formed by the interaction of CO with Co<sup>2+</sup> and Co<sup>3+</sup> ions, respectively.<sup>[29]</sup>

The IR spectrum of the LaFeO<sub>x</sub>/ZrO<sub>2</sub> sample demonstrates the low-intensity absorption band at 2171 cm<sup>-1</sup>, main bands at 2086 and 2058 cm<sup>-1</sup>, and shoulders at 1997 cm<sup>-1</sup> after CO adsorption. The position of the first absorption band shows that this band most likely belongs to CO complexes with low-coordinated Fe ions Fe<sup>2+</sup> and/or Fe<sup>3+</sup>.<sup>[28]</sup> The change in the oxidation state of Fe caused by the change in the oxidation state of Fe is in agreement with the literature data on the loss of a part of mobile oxygen by perovskites upon high-temperature annealing,<sup>[29]</sup> presumably owing to the LaFe<sup>3+</sup>O<sub>3</sub>→LaFe<sup>2+</sup>O<sub>2.5</sub> transition. The band at 2086 cm<sup>-1</sup> may be assigned to the monocarbonyl species Fe<sup>2+</sup>–CO.<sup>[28,29]</sup> The bands at 2058 and 1997 cm<sup>-1</sup> are most likely characteristic of the binuclear carbonyl group [Fe<sup>2+</sup>–(CO)–Fe<sup>2+</sup>].

The IR spectrum of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample demonstrates absorption bands at 2086, 2005, and 1915 cm<sup>-1</sup> (main bands) and shoulders at 1970 and 1890 cm<sup>-1</sup> after CO adsorption. The position of the first absorption band indicates that this band most likely belongs to CO complexes with low-coordinated Ni ions Ni<sup>2+</sup>, which is in agreement with the literature data showing, in addition, that low-coordinated Ni ions Ni<sup>3+</sup> do not form carbonyl species.<sup>[28]</sup> These data are in agreement with the literature data on the loss of a part of mobile oxygen by perovskites upon high-temperature annealing,<sup>[29]</sup> presumably owing to the LaNi<sup>3+</sup>O<sub>3</sub>→LaNi<sup>2+</sup>O<sub>2.5</sub> transition. The doublet bands at 2005, 1970 cm<sup>-1</sup> and 1915, 1890 cm<sup>-1</sup> may be assigned to the asymmetric and symmetric bands of the bridged dicarbonyl species Ni(CO)<sub>2</sub> formed by the interaction of CO with Ni<sup>2+</sup> ions.<sup>[28]</sup>

The oxidation state of low-coordinated ions in LaCoO<sub>x</sub>/ZrO<sub>2</sub>, LaFeO<sub>x</sub>/ZrO<sub>2</sub>, and LaNiO<sub>x</sub>/ZrO<sub>2</sub> was also studied through the adsorption of deuteroacetonitrile used as a probe. The DRIFT spectra of adsorbed CD<sub>3</sub>CN are shown in Figure 3. The bands of the stretching vibrations of the C=N group at 2281 and 2266 cm<sup>-1</sup> in the spectrum of LaCoO<sub>x</sub>/ZrO<sub>2</sub> can be attributed to CD<sub>3</sub>CN complexes, with perovskite nanoparticles attributed to the interaction with coordinatively unsaturated Co<sup>3+</sup> (2281 cm<sup>-1</sup>) and Co<sup>2+</sup> (2266 cm<sup>-1</sup>) ions, that is, Lewis acid sites of the moderate and low strength, respectively. The blueshift of the C=N stretching vibration is 28 and 13 cm<sup>-1</sup>, which is similar to that of gas-phase acetonitrile.<sup>[30]</sup> This conclusion agrees fairly well with the data obtained in studying CO adsorption on these samples. The differences in the relative intensities of the bands corresponding to the complexes with Co<sup>3+</sup> and Co<sup>2+</sup> ions observed in the spectra of CO and CD<sub>3</sub>CN may be due to the differences in the extinction coefficients of these molecules. The extinction coefficient of adsorbed CO increases significantly with the increase in the frequency shift toward higher frequencies, whereas for acetonitrile the changes in the extinction coefficient are much less significant.<sup>[31]</sup> Notably, the spectra of acetonitrile adsorbed on Lewis acid sites of ZrO<sub>2</sub> described in the literature<sup>[27]</sup> contain only one band at 2300-2295 cm<sup>-1</sup>, which coincides with a shoulder observed in the spectra of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample.

The broad absorption band of the stretching vibration of the C=N group at 2266 is observed in the spectra of LaFeO<sub>x</sub>/ ZrO<sub>2</sub> and LaNiO<sub>x</sub>/ZrO<sub>2</sub>, which can be ascribed to CD<sub>3</sub>CN complexes with low-coordinated metal ions, as well as the band at 2106 cm<sup>-1</sup> corresponding to the stretching vibration of the C-D group. The band at 2266 cm<sup>-1</sup> observed in the spectra of the LaFeO<sub>x</sub>/ZrO<sub>2</sub> and LaNiO<sub>x</sub>/ZrO<sub>2</sub> samples can be attributed to acetonitrile complexes with coordinatively unsaturated Fe<sup>2+</sup>

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and Ni<sup>2+</sup> ions, that is, Lewis acid sites of low strength. The blueshift of the C=N stretching vibration is 13 cm<sup>-1</sup>, which is similar to that of gas-phase acetonitrile.<sup>[30]</sup> This conclusion agrees fairly well with the data obtained in studying CO adsorption on the same samples.

In addition, an intense band at 2173 cm<sup>-1</sup> is observed in the spectra of both LaFeO<sub>x</sub>/ZrO<sub>2</sub> and LaNiO<sub>x</sub>/ZrO<sub>2</sub> samples. This band can be associated with the stretching vibration of the C= C=N skeleton in a ketene imine molecule that is a tautomer of CD<sub>3</sub>-C=N.<sup>[32,33]</sup>

Thus, by using DRIFT spectroscopy with adsorbed probe molecules, it was found that coordinatively unsaturated Co, Fe, and Ni ions are present on the surface of the systems representing mesoporous zirconia with supported  $LaCoO_x$ ,  $LaFeO_x$ , and  $LaNiO_x$  nanoparticles.

#### X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) survey spectra of the surface and subsurface layers ( $\approx$  30 Å) are shown in Figure 4. C1s, O1s, La3d, La4d, Zr3d, Zr3p, and Zr3s photo-



Figure 4. XPS survey spectra of the LaCoO\_x/ZrO\_2, LaFeO\_x/ZrO\_2, and LaNiO\_x/ZrO\_ samples.

electron lines and C KLL, O KVV, and La MNN Auger electron lines are observed in the spectra of supported perovskites. In addition, Co2p photoelectron and Co LMM Auger electron lines are observed in the spectrum of  $LaCoO_x/ZrO_2$ ; the Fe2p photoelectron line in the spectrum of  $LaFeO_x/ZrO_2$ ; and the Ni2p photoelectron line overlapped with the La3d photoelectron line and Ni LMM Auger electron lines in the spectrum of LaNiO\_x/ZrO\_2.

The binding energies (BEs) of photoelectron lines and surface atomic ratios for  $LaCoO_x/ZrO_2$ ,  $LaFeO_x/ZrO_2$ , and  $LaCoNi_x/ZrO_2$  samples are given in Table 1.

The XPS data indicate the BE of the Co  $2p_{3/2}$  doublet component to be 780.9 eV as well as the presence of satellites characteristic of Co cations. From these data, one can conclude that Co in the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample exists in surface layers, most likely in both 2+ and 3+ oxidation states. The BE of the Fe  $2p_{3/2}$  component, 711.1 eV, is indicative of the existence of

Table 1. XPS data of the LaCoO <sub>x</sub> /ZrO <sub>2</sub> , LaFeO <sub>x</sub> /ZrO <sub>2</sub> , and LaNiO <sub>x</sub> /ZrO <sub>2</sub> samples.							
Perovskite	Bindin O 1 s	g energy Zr 3d <sub>5/2</sub>	[eV] M <sup>[a]</sup> 2p <sub>3/2</sub>	La 3d <sub>5/2</sub>	Atomic M <sup>[a]</sup> /Zr	ratio La/Zr	M <sup>[a]</sup> /La
LaCoO <sub>x</sub> LaFeO <sub>x</sub> LaNiO <sub>x</sub>	530.5 530.1 530.9	182.4 182.3 182.3	780.9 711.1 854.5	834.4 834.7 834.6	0.206 0.139 0.409	0.344 0.350 0.397	0.599 0.397 0.259
[a] M=Co, Fe, and Ni.							

Fe in the surface layers of the LaFeO<sub>x</sub>/ZrO<sub>2</sub> sample, most likely in two oxidation states (Fe<sup>2+</sup> and Fe<sup>3+</sup>). The BE of the Ni2p<sub>3/2</sub> component, 855.0 eV, derived by the deconvolution of the La3d+Ni2p<sub>3/2</sub> electron spectrum shows that Ni in the surface layers of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample also exists, most likely in two oxidation states (Ni<sup>2+</sup> and Ni<sup>3+</sup>).

The data derived from XPS analysis about the electronic states of Co, Fe, and Ni are in good agreement with the data derived from DRIFTS analysis.

The surface atomic ratio M/La (M=Co, Fe or Ni) differs from unity, which indicates the migration of La to the surface layers or conversely the migration of Co, Fe, and Ni to the bulk of supported perovskite microcrystals.

The BE of the La3d<sub>5/2</sub> component, 834.4–834.7 eV (Table 1), is characteristic of the La<sup>3+</sup> oxidation state, and the BE of the Zr3d<sub>5/2</sub> component, 182.3–182.4 eV, is specific for the Zr<sup>4+</sup> oxidation state in supported perovskite samples.

#### X-ray absorption spectroscopy

The Co K-edge X-ray absorption near edge structure (XANES) spectra of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample and reference compounds are shown in Figure 5 a, which demonstrates that the spectrum of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample differs from those of the Co foil and CoO references and resembles the spectrum of a Co<sub>3</sub>O<sub>4</sub> spinel reference. At the same time, the energetic position of the Co K-edge absorption spectrum of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample is higher than that of the spectrum of Co<sub>3</sub>O<sub>4</sub>. This observation indicates that the main part of Co in these samples exists in the Co<sup>3+</sup> oxidation state. These data agree with the XPS data that indicate the presence of both Co<sup>2+</sup> and Co<sup>3+</sup> cations. The Co K-edge extended X-ray absorption fine structure (EXAFS) spectra of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample and reference compounds are shown in Figure 5b, which demonstrates that the EXAFS spectrum of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample differs from the spectra of Co foil, CoO, and Co<sub>3</sub>O<sub>4</sub> spinel references. The first peak at an uncorrected distance of approximately 1.5 Å is observed in the spectrum of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample. The position of this peak is close to that in the spectrum of the spinel and is lower than that in the spectrum of CoO. This peak corresponds to oxygen atoms as nearest neighbors to the central Co atom. The second peak is located at the same distance as the second peak in the spectrum of Co<sub>3</sub>O<sub>4</sub> and corresponds to the next Co-O atomic pair. The third peak locates at a distance higher than that of the first peak in the Co foil spectrum, the second peak in the CoO spectrum, and the third peak in the

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Figure 5. Normalized Co K-edge a) XANES and b) EXAFS spectra of the  $LaCoO_x/ZrO_2$  sample and reference compounds.

Co<sub>3</sub>O<sub>4</sub> spectrum. Therefore, this peak reflects the presence (as a third neighbor) of atoms heavier than Co atoms, for example, La atoms. The average local structure of Co atoms in the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample obtained from the model fit of EXAFS data is presented in Table 2. The processing of the EXAFS data of the LaCoO<sub>x</sub>/ZrO<sub>2</sub> sample demonstrates that the nearest neighbors of the central Co atom are an average number of  $3.2\pm0.3$  oxygen atoms at an average real distance of  $1.93\pm0.01$  Å. The second shell contains an average number of  $2.87\pm0.03$  Å. The third coordination shell contains an average number of  $2.2\pm0.3$  La atoms at an average real distance of  $3.39\pm0.01$  Å.

Table 2. EXAFS data of the LaCoO_/ZrO_ and LaNiO_/ZrO_ samples.					
Sample	Atomic pair	r [Å]	Coordination number	$\lambda^{2}$ [10 <sup>-3</sup> Å <sup>2</sup> ]	Δ <i>Ε</i> [eV]
LaCoO <sub>x</sub> / ZrO <sub>2</sub>	Co0	1.93±0.01	3.2±0.3	4±1	16±1
	Co–O	$2.87\pm0.03$	$1.4 \pm 0.5$	$1\pm1$	$15\pm1$
	Co–La	$3.39\pm0.01$	$2.2\pm0.3$	$9\pm1$	$29\pm2$
LaNiO <sub>x</sub> / ZrO <sub>2</sub>	Ni–O	$2.09 \pm 0.01$	$5.2\pm0.5$	12±2	$24\pm1$
	Ni–Ni	$2.92\pm0.01$	$3.9\pm0.7$	$7\pm1$	$10\pm 1$
	Ni—La	3.16±0.01	6.9±0.9	8±1	$29\pm1$



Figure 6. Normalized Ni K-edge a) XANES and b) EXAFS spectra of the LaNiO $_x$ /ZrO $_2$  sample and reference compounds.

Notably, the local structure of Co atoms in the  $LaCoO_x/ZrO_2$  sample differs from that of the Co atom in unsupported  $LaCoO_3$ , the crystallographic data of which were used for the FEFF file.

The Ni K-edge XANES spectra of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample and reference compounds are shown in Figure 6a, which demonstrates that the spectrum of this sample differs from that of the Ni foil reference and resembles that of an NiO reference. At the same time, the energetic position of the Ni K-edge absorption spectrum of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample is higher and the intensity of the white line is lower than that for NiO. This finding indicates that the electronic state and local structure of Ni atoms in the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample differ from those of NiO. These data agree with the XPS data that indicate the presence of both Ni<sup>2+</sup> and Ni<sup>3+</sup> cations.

The Ni K-edge EXAFS spectra of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample and reference compounds are shown in Figure 6b, which demonstrates that the EXAFS spectrum of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample differs from that of the Ni foil and resembles the spectrum of NiO. The first peak is situated at an uncorrected distance of approximately 1.5 Å in the spectrum of the LaNiO<sub>x</sub>/ZrO<sub>2</sub> sample. The distance of this peak in the spectrum of the supported perovskite is slightly shorter than that in the spectrum of NiO. This peak corresponds to oxygen atoms as nearest neighbors to the central Ni atom, and its intensity is lower in the spectrum of the supported perovskite. The second peak is situated

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at roughly the same distance as the second peak in the spectrum of NiO and corresponds to the Ni–Ni atomic pair. The average local structure of Ni atoms in the LaNiO<sub>3</sub>/ZrO<sub>2</sub> sample obtained from the model fit of EXAFS data is presented in Table 2. The calculation of the EXAFS data of the LaNiO<sub>3</sub>/ZrO<sub>2</sub> sample demonstrates that the nearest neighbors of the central Ni atom are an average number of  $5.2\pm0.5$  oxygen atoms at an average real distance of  $2.09\pm0.01$  Å. The second shell contains an average number of  $3.9\pm0.7$  Ni atoms at an average real distance of  $2.92\pm0.01$  Å. The third coordination shell contains an average number of  $6.9\pm0.9$  La atoms at an average real distance of  $3.16\pm0.01$  Å. Thus, the local structure of Ni atoms in perovskites supported on ZrO<sub>2</sub> differs from that of the Ni atom in unsupported LaNiO<sub>3</sub>, the crystallographic data of which were used for the FEFF file.

#### **Catalytic activity**

The prepared catalysts were tested in the reaction of oxidation of a gas mixture containing CO and oxygen.

The change in CO conversion with the increase in temperature over the Co, Ni, and Fe perovskites supported on mesoporous zirconia is shown in Figure 7. The turnover frequencies for the three studied perovskites are given in Table 3.



Figure 7. CO oxidation over the zirconia-supported perovskites.

Table 3. Turnover frequencies for CO oxidation at 50% conversion.					
Sample	<i>T</i> <sub>50% conv.</sub> [°C]	Turnover frequency [h <sup>-1</sup> ]			
LaNiO <sub>x</sub> /ZrO <sub>2</sub>	300	34.1			
LaCoO <sub>x</sub> /ZrO <sub>2</sub>	200	30.9			
LaFeO <sub>x</sub> /ZrO <sub>2</sub>	300	37.2			

The following order of the activity in CO oxidation, based on the temperature of the 50% conversion, was found in the temperature range 50–400 °C: LaCoO<sub>3</sub>/ZrO<sub>2</sub> (200 °C) > LaFeO<sub>3</sub>/ZrO<sub>2</sub> (275 °C) > LaNiO<sub>3</sub>/ZrO<sub>2</sub> (300 °C).

However, the Ni-containing catalyst demonstrates a higher activity in CO oxidation in the low-temperature range as compared with the Fe-containing catalyst and the temperatures of

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the 10% conversion follow a different trend:  $LaCoO_3/ZrO_2$ (165 °C) >  $LaNiO_3/ZrO_2$  (180 °C) >  $LaFeO_3/ZrO_2$  (210 °C).

## Conclusions

The nanoparticles of perovskites with different transition metal ions (Ni, Co, Fe) based on La were supported on mesoporous zirconia and demonstrated high activity in CO oxidation because LaCoO<sub>3</sub> was the most active of all the perovskites studied. In complete oxidation, the use of non-noble metal catalysts with activities comparable to or even lower than those of the conventional Pd or Pt catalysts is quite challenging because it enables one to dramatically reduce the cost of the catalysts for environmental applications without sacrificing the performance (activity) of the materials.

## **Experimental Section**

#### Preparation of LaMO<sub>3</sub>/mesoporous ZrO<sub>2</sub>

The synthesis of mesoporous zirconia was performed according to the previously developed and modified method.<sup>[20]</sup> A 15% solution of cetyltrimethylammonium bromide (CTMABr) was prepared by dissolving CTMABr (19.7 g) in acidified water (110 mL, pH 2.0) at 40 °C and mixing the solution for 3 h. Then, a 70% solution of zirconium isopropoxide in 2-propanol (76 g) was added to the CTMABr solution under rigorous stirring (CTMABr/Zr molar ratio = 0.33:1.0). The mixture was stirred for 1 h at 40 °C and then placed in an autoclave with Teflon lining and heated at 60 °C for 48 h. The precipitate was filtered off, washed multiple times with ethanol, and dried in air at 75 °C for 48 h. The obtained zirconium dioxide ( $\approx$ 10 g; yield:  $\approx$ 50%) was calcined in flowing air at 600 °C.

A glycine complex of La and Co/Fe/Ni was prepared by the recipe described in Refs. [21and22]. For this purpose, La and Co/Fe/Ni nitrates taken in equimolar amounts ([La]=0.005 mol; [M]= 0.005 mol) were dissolved in distilled water (50 mL). After the complete dissolution of the salts, an aqueous glycine solution (50 mL; 0.05 mol of glycine) was added. The molar ratio of glycine to the sum of cations was 5:1.

The samples of supported La-metal perovskites (LaMO<sub>x</sub>, M = Co, Ni, Fe) were prepared through the impregnation of the precalcined mesoporous carrier (ZrO<sub>2</sub>) with a solution of the prepared La-Co/Fe/Ni glycine complex. Some amount (1.5 g) of the air-dried support was impregnated with the aqueous solution of the precursor (10 mL), which corresponds to the supported perovskite ( $\approx$ 10 wt%). Then, the sample was dried at 60–65 °C and calcined in air at 400 or 600 °C for 8 h. The sample prepared on the basis of the carrier precalcined at 600 °C was annealed at 600 °C.

#### Characterization of the samples

The chemical analysis of the samples for the contents of the metals (Zr, Co, Ni, Fe, and La) was performed by using atomic emission spectroscopy. The sample loading was dissolved in a hot mixture of concentrated acids HF, HNO<sub>3</sub>, and HCl. Furthermore, the solution was evaporated and the solid was dissolved in HCl. After repeating this method twice, the obtained solution was analyzed for La, Co, Ni, Fe, and Zr within the accuracy of  $\pm 3$  rel.%.

The DRIFT spectra were recorded at RT in the frequency range of 6000–400  $\rm cm^{-1}$  with a resolution of 4  $\rm cm^{-1}$  on a NICOLET Protege

460 spectrometer equipped with a diffuse reflectance attachment developed earlier at the N.D. Zelinsky Institute of Organic Chemistry, Moscow.<sup>[23]</sup> To have a satisfactory signal-to-noise ratio, 500 spectra were collected.  $CaF_2$  powder was used as a reference. Before the spectroscopic measurements, the samples were evacuated at 400 °C for 2 h to remove physically adsorbed water. The following probe molecules were used to test surface sites of different nature: CO as a probe for Lewis acid sites and low-coordinated metal ions, and CD<sub>3</sub>CN as a probe for both Lewis and Brønsted (if present) acid sites. The probe molecules were adsorbed at RT and an equilibrium pressure of 5 Torr (1 Torr = 133.3 Pa) for CO and of 96 Torr for CD<sub>3</sub>CN (saturated pressures).

The phase composition of the samples and the particle size of the supported metal were determined from XRD analysis. The XRD patterns were recorded with a DRON-2 diffractometer with Ni-filtered CuK<sub>α</sub> radiation ( $\lambda$ =0.1542 nm) in a step-scanning mode, with a step size of 0.02° and a counting time of 0.6 step<sup>-1</sup> at 2 $\theta$ =10–85°. All major reflections were covered in this scan range. The phases were identified by comparing the position and intensity of the lines with the data from the files of the International Center for Diffraction Data. To estimate precisely the average particle size of the phases, the diffraction patterns were recorded at 2 $\theta$ =35–50°, with a step size of 0.02° and a counting time of 1.2 step<sup>-1</sup>. The crystal sizes of the nanoparticles were determined from X-ray line broadening analysis.

The X-ray absorption (XANES and EXAFS) spectra (Co K edge at 7709 eV and Ni K edge at 8333 eV) were measured at the Hasylab X1 station (Hamburg, Germany) with a Si(111) double crystal monochromator. The spectra were recorded in the transmission mode at -196 °C. The spectrum of the Co or Ni foil was registered simultaneously between the second and third ionization chambers for energy calibration. The EXAFS data analysis was performed with the VIPER software.<sup>[24]</sup> The reference spectra were recorded by using standard reference compounds: CoO, Co<sub>3</sub>O<sub>4</sub>, Co foil, NiO, and Ni foil. The required scattering amplitudes and phase shifts were calculated with the ab initio FEFF8.10 code.<sup>[25]</sup> Fitting was performed in the *k* and *r* spaces.

The XPS spectra were recorded with a XSAM 800 spectrometer with a MgK<sub> $\alpha$ </sub> X-ray (1253.6 eV) source. The base pressure in the XPS chamber was approximately 10<sup>-9</sup> Torr. The spectrometer was calibrated by the BE of the Au4f<sub>7/2</sub> component (84.0 eV) and the Ni2p<sub>3/2</sub> component (852.7 eV). The XPS survey spectra were collected between 20 and 1130 eV. The detailed spectra were recorded for the region of C1s, O1s, Co2p, Ni2p, Ni3p, Fe2p, La3d, and Zr3d, with a step size of 0.1 eV. The C1s line at 285.0 eV was used as the internal standard. The surface atomic composition was calculated by using the photoionization cross sections.

#### Catalyst testing in CO oxidation

The synthesized powders were pressed into discs in a stainless steel module (diameter: 15 mm) under a hydraulic pressure of 10 MPa. The tablets were then crushed and sieved into particles of sizes ranging from 0.25 to 0.1 mm for characterization and catalytic tests. Catalyst testing was performed in a laboratory-scale fixed-bed quartz reactor (internal diameter: 3 mm) operating at an atmospheric pressure. The catalyst was placed on a thin layer of quartz wool in the reactor. In each test, the catalyst volume was 0.1 cm<sup>3</sup>. Before testing, each catalyst was pretreated in a dry air flow at 300 °C for 1 h to remove water and adsorbed impurities, and then the reactor was cooled to RT. The reactor temperature was monitored with a thermocouple in the catalyst layer. The activ-

ity tests were performed at different temperatures, ranging from 50 to 500 °C. The temperature in the reactor was ramped with a step size of 50 °C until a 100% CO conversion was achieved. After that, the temperature was decreased stepwise to return to the starting point of the conversion cure at which zero conversion was observed. The feed gas mixture consisted of 4.5 vol% CO, 22.5 vol%  $O_{2r}$  and He balance. The total feed flow rate was held constant at 10 cm<sup>3</sup>min<sup>-1</sup>, with a volume hourly space velocity of 6000 h<sup>-1</sup>. The turnover frequency was calculated as the number of moles of CO converted per mole of the supported peroxide per hour.

The effluent gas mixture from the reactor was analyzed with a gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5A column to determine CO conversion.

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