Characterization and carbon monoxide oxidation activity of 
La$_{1-x}$Sr$_x$Cr$_1$-xRu$_x$O$_3$ perovskites

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The oxidation of CO over La$_{1-x}$Sr$_x$Cr$_1$-xRu$_x$O$_3$ perovskite type oxides with \( y=0.3 \)
and \( 0 \leq x \leq 0.100 \) have been studied. X-ray fluorescence analysis confirmed that content
of elements in the bulk corresponds to the established nominal perovskite stoichiometry,
indicating that no significant oxidation of ruthenium into volatile polyvalent oxides with
their consequent escape from the sample occurred in air up to the temperature of
1000 °C. According to X-ray diffraction analysis, all samples achieved the perovskite
hexagonal with the presence of some SrCrO$_3$. X-ray photoelectron spectroscopy analysis
of ruthenium samples shows higher Ru and Sr surface concentrations than in the
bulk. The binding energy for Ru$_{3d}$ is virtually the same in all samples and consistent
with that of Ru$^{4+}$ (463.6–464.3 eV). Kinetic studies were performed in a differential
recycle reactor with a recycling ratio 80. The results show that substitution of Ru$^{4+}$ for
Cr$^{3+}$ in La$_{1-x}$Sr$_x$Cr$_1$O$_3$ leads to a significant increase in both the activity and the activation
energy. The global CO oxidation rate, referred on the BET surface area, correlates with
the surface Ru$^{4+}$ atomic concentration. Hence, the activity reflect the surface enrichment
in ruthenium. Moreover, an identical apparent activation energy \( E = 93 \) kJ/mol and the
same specific rate per ruthenium surface ion were obtained for samples with a Ru content
\( x > 0.05 \) suggest that exposed Ru$^{4+}$ ions mainly participate in the reaction.

Keywords: perovskite, ruthenium, CO oxidation.

Studies of perovskite type catalysts (ABO$_3$) with a rare earth ion in the A site
and a transition metal ion in the B site have concentrated on the complete oxidation
of CO and hydrocarbons and reduction of NO$_x$ particularly related to auto exhaust
control.$^1,2$

In our previous papers$^3$–$^5$ we reported on the activity of a series of LaMO$_3$
\( (M = \text{Co, Cr and Cu}) \) perovskites and mixed oxides La$_{1-x}$Sr$_x$MO$_3$ \( (M = \text{Cr and Ru}) \)
in the simultaneous oxidation of CO and hydrocarbons and reduction of NO$_x$ with
controlled compositions of the gas mixture around the stoichiometric ratio of
oxidizing to reducing agents. The investigations were performed in a pulse-flame catalytic system with a feed gas obtained by combustion of 2,2,4-trimethylpentane (isooctane) containing about 11 vol.% of H₂O and also in a dry synthetic gas mixture. According to the results on La₁₋ₓSrₓCr₁₋ₓRuₓO₃ (0.05 ≤ x ≤ 0.100) mixed oxides, under net reducing conditions, an unexpected higher conversion of CO and a higher concentration of hydrogen in the outlet reaction gases were obtained in the presence of water vapor compared to those observed in the synthetic dry reaction mixture. These effects were ascribed to the water-gas shift reaction, catalyzed by ruthenium ions. Furthermore, the hydrogen formed in the water gas shift reaction, absorbed on the surface in the dissociative form, could be a reason for the high conversion of NOₓ observed on ruthenium perovskites under net oxidizing conditions.

This paper presents the CO oxidation activity of perovskite type oxides La₁₋ₓSrₓCr₁₋ₓRuₓO₃ with y = 0.3 and 0 ≤ x ≤ 0.100. The results are discussed in relation to the bulk and surface composition and the oxidation state of the cations in samples with different Ru content.

**EXPERIMENTAL**

*Catalyst preparation*

A series of perovskite type oxides La₁₋ₓSrₓCr₁₋ₓRuₓO₃ containing a constant content of Sr (y = 0.3) and with x ranging from 0 to 0.100 was prepared from La₂O₃, Cr₂O₃, RuO₂ and SrCO₃ of analytical grade quality by solid-state processing. The respective amounts of the constituent oxides and carbonates were mixed in ethanol and sintered. The temperature of calcination was increased stepwise up to 1000 °C. Cycles of grinding and heating were performed at the chosen temperatures to ensure homogeneity and to complete the reaction.

*Characterization of catalyst*

The chemical composition of the samples was determined by X-ray fluorescence analysis (XRF), using a System Camerino Model 7333E. The phase composition of the samples was investigated by X-ray diffraction analysis (XRD) of powdered samples using a Philips PW 1710 diffractometer, with CuKα graphite-monochromatized radiation (40 kV, 30 mA). The lattice constants were calculated by the least squares method (program LUSCRPC). X-ray photoelectron spectra (XPS) were recorded on a VG Escalab II spectrometer with MgKα radiation (1253.6 eV) at a pressure of 4·10⁻¹¹ Torr and an instrumental resolution for Ag 3d₃/₂ line 0.9 eV. The normalized XPS intensities 1/s, which are proportional to the effective concentrations of the corresponding elements in the surface layers, were determined as the integrated peak areas divided by the corresponding photon ionization cross section. In the peak area computation, the background was assumed to be linear.

The specific surface area of the samples was measured using the BET method.

*Catalytic tests*

The kinetics of carbon monoxide oxidation was measured in an integrated-external recycle reactor. A detailed description of the apparatus has been given elsewhere. A gas reaction mixture containing 1 vol.% CO and 1 vol.% O₂ was fed at constant flow rate of 10 l/h. The recycling ratio of 80 was maintained constant to obtain gradientless conditions in all catalytic runs. The gas composition was analyzed before and after the reaction by an online gas chromatograph (Shimadzu GC-8A) interfaced with an automatic integrator. The global reaction rate was calculated using the equation:

\[ r = \left( \frac{c_f}{c_i} - \frac{c_f}{c_i} \right) \cdot F \]
where $c_{\text{in}}$ and $c_{\text{out}}$ are the concentration of CO (vol.% in the inlet and the outlet, respectively, $w$ is the mass (g) of catalyst, and $F$ is the feed flow rate (cm$^3$/s).

RESULTS AND DISCUSSION

The atomic concentrations of elements in the bulk (XRF) and the surface layers (XPS) of the ruthenium perovskite are given in Table 1.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Bulk concentration (at.%)</th>
<th>Surface concentration (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
<td>Sr</td>
</tr>
<tr>
<td>0.025</td>
<td>14.0</td>
<td>60</td>
</tr>
<tr>
<td>0.050</td>
<td>14.0</td>
<td>60</td>
</tr>
<tr>
<td>0.075</td>
<td>14.0</td>
<td>60</td>
</tr>
<tr>
<td>0.100</td>
<td>14.0</td>
<td>60</td>
</tr>
</tbody>
</table>

The content of elements in the bulk corresponds to the composition of the initial mixture of the samples, i.e., to the nominal perovskite stoichiometry La$_{1-y}$Sr$_y$Cr$_1$O$_3$ with $y = 0.3$ and $x$ varying in the range 0.025 $\leq x \leq$ 0.100. Moreover, the very good agreement between the amounts of ruthenium taken and those found in the systems obtained after heating at 1000 °C in air, indicates that no significant oxidation of ruthenium into volatile polyvalent oxides RuO$_3$ and RuO$_4$ and their consequent escape from the sample occurred under the oxidation conditions. This is the main problem in the case of supported ruthenium catalysts. In the following figures and tables all the synthesized ruthenium perovskite catalysts are denoted according to the nominal perovskite stoichiometry.

On the XRD pattern (Fig. 1) of the sample without Sr, only perovskite phase LaCrO$_3$ was identified. The unambiguous phase identification of a few very weak peaks was not possible. The X-ray diffraction peaks of LaCrO$_3$ were completely indexed from a cubic symmetry with lattice parameter $a = 3.8847(6)$ Å. In all samples with La partly substituted by Sr in A site, however, weak diffraction peaks attributed to SrCrO$_4$ were detected together with the perovskite ones. Thermal treatment of the samples in air resulted in the oxidation of part of the Cr$^{3+}$ to Cr$^{6+}$ which reacted with strontium carbonate forming a SrCrO$_4$ phase. In the ruthenium containing samples no peaks corresponding to RuO$_2$ or other component single oxides were detected. Since, according to chemical analysis, almost all ruthenium remained in the samples, the formation of very small RuO$_2$ particles, which could not be detected by XRD, due to their strong tendency to volatilization under oxidizing conditions, can be excluded. Hence, it can be considered that the ruthenium is incorporated in the perovskite structure.

The formation of SrCrO$_4$ as a separate phase implies a decrease in the Sr and Cr content in the perovskite phase.
Fig. 1. XRD powder patterns of La_{1-x}Sr_xCr_{10-x}Ru_xO_{13} (0.025 ≤ x ≤ 0.100).

Fig. 2. Photoelectron spectra of Cr_{2p} of La_{1-x}Sr_xCr_{10-x}Ru_xO_{13} (0.025 ≤ x ≤ 0.100).
The Cr\textsubscript{2p} photoelectron spectra (Fig. 2) exhibit two peaks with BE of 576.5 eV and 579.9 eV, characteristic for Cr\textsuperscript{3+} and Cr\textsuperscript{6+}, respectively. Standardization of the peaks gave about 20% contribution of Cr\textsuperscript{6+} to the total amount of chromium in the surface layers in all synthesized samples. This is in good agreement with the estimation of the relative bulk content of the SrCrO\textsubscript{4} phase.

The absence of other isolated phases of the individual oxides, which should crystallize out at the calcination temperature of 1000\degree C, implies that chromium and equivalent amounts of strontium are distributed in the perovskite and strontium chromate phases. Assuming that 20% of the total amount of Cr (all the formed Cr\textsuperscript{6+}) and an equivalent amount of Sr\textsuperscript{2+} are bonded in SrCrO\textsubscript{4} the calculated average content of Sr in the \( \text{La}_1-y\text{Sr}_y\text{Cr}_{1-x}\text{Ru}_x\text{O}_3 \) perovskite phase significantly decreases from \( y = 0.3 \) to \( y = 0.14 \). Accordingly the La/Sr ratio in the perovskite phase increases from a nominal 2.33 to 6.14.

This is consistent with the lattice parameters of the perovskites \( \text{La}_1-y\text{Sr}_y\text{Cr}_{1-x}\text{Ru}_x\text{O}_3 \), which are given in Table II.

| Table II. The unit cell parameters of the perovskite phase occurring in the synthesized \( \text{La}_1-y\text{Sr}_y\text{Cr}_{1-x}\text{Ru}_x\text{O}_3 \) samples |
|---|---|---|---|---|
| The composition of the initial mixtures | Lattice parameters | Volume (\( \text{Å}^3 \)) | Reference |
| \( y \) | \( x \) | \( a(\text{Å}) \) | \( c(\text{Å}) \) | |
| 0 | 0 | 5.494\textsuperscript{4} | 13.458\textsuperscript{6} | 352 \( \pm \)58.62(3) | this paper |
| 0.3 | 0.00 | 5.482(5) | 13.454(9) | 351.4(4) | this paper |
| 0.3 | 0.07 | 5.478(4) | 13.495(9) | 350.7(4) | this paper |
| 0.3 | 0.05 | 5.474(4) | 13.48(1) | 349.7(5) | this paper |
| 0.3 | 0.025 | 5.475(4) | 13.488(7) | 350.2(3) | this paper |
| 0.3 | 0 | 5.466(3) | 13.49(1) | 349.2(4) | this paper |
| 0.25 | 0 | 5.493-0.002\textsuperscript{5} | 13.301-0.006 | 348 | JCPDS 32-1240 |

\textsuperscript{4}Calculated from cubic cell with \( a = 3.8847(6) \text{ Å} \) using equations \( a = \sqrt[3]{a} \cdot (2)\textsuperscript{1/2} \) and \( c = \sqrt[3]{a} \cdot (3)\textsuperscript{1/2}/2 \). 
\textsuperscript{5}Actually, 5.403-0.002 Å was reported (Khantak,\textsuperscript{14}) but this is probably a typing error, because the calculated parameter of the hexagonal unit cell from the rhombohedral lattice parameters is \( a = 2 \cdot 5.451 \cdot \sin(30.255) \cdot 5.493 \text{ Å} \).

The observed diffraction peaks of the perovskite phase are mostly broad and asymmetric but not split very well suggesting that the perovskite lattice is slightly distorted compared to an ideal cubic structure. The lattice parameters of the hexagonal perovskite unit cell are very similar for all investigated samples. Moreover, their unit cell volumes are between the LaCrO\textsubscript{3} and the La\textsubscript{0.75}Sr\textsubscript{0.25}CrO\textsubscript{3} volume.\textsuperscript{14} This is in agreement with the previous conclusion concerning the formation of the perovskite phase with a lower content of Sr (\( y = 0.14 \)) than expected (\( y = 0.3 \)) according to the overall metal content (Table I).

The Cr\textsubscript{2p} binding energy values for Cr\textsuperscript{3+} and Cr\textsuperscript{4+} are very close. Therefore, the separation of the peaks was not possible with the resolution of instrument used. Decon-
volution of the Cr$^{3+}$ peak, which is broad and asymmetric (Fig. 2), performed for the sample $x = 0.075$, might be an indication of the possible presence of Cr$^{4+}$ ions (Fig. 3).

The binding energy for Ru$_{3p}$ (463.6–464.3 eV) is virtually the same in all samples and it is consistent with that of Ru$^{4+}$ (Fig. 4).
The calculated composition of the perovskite phases in the La$_{1-x}$Sr$_x$Cr$_{1-x}$Ru$_x$O$_3$ samples was made assuming that all Ru is incorporated in the perovskite and is presented in Table III.

**TABLE III. Calculated composition of perovskite La$_{1-x}$Sr$_x$Cr$_{1-x}$Ru$_x$O$_3$ phases**

<table>
<thead>
<tr>
<th>$x$</th>
<th>Calculated composition of the perovskite phases</th>
<th>cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\text{La}^{3+} \cdot 0.875 \text{Sr}^{2+} \cdot 0.125 \text{Cr}^{3+} \cdot \text{O}_6$</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>$\text{La}^{3+} \cdot 0.375 \text{Sr}^{2+} \cdot 0.625 \text{Cr}^{3+} \cdot 0.875 \text{Cr}^{4+} \cdot 0.125 \text{O}_6$</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>$\text{La}^{3+} \cdot 0.869 \text{Sr}^{2+} \cdot 0.131 \text{Cr}^{3+} \cdot 0.969 \text{Ru}^{4+} \cdot 0.031 \text{O}_6$</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>$\text{La}^{3+} \cdot 0.386 \text{Sr}^{2+} \cdot 0.614 \text{Cr}^{3+} \cdot 0.980 \text{Cr}^{4+} \cdot 0.020 \text{O}_6$</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>$\text{La}^{3+} \cdot 0.865 \text{Sr}^{2+} \cdot 0.135 \text{Cr}^{3+} \cdot 0.965 \text{Cr}^{4+} \cdot 0.035 \text{O}_6$</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>$\text{La}^{3+} \cdot 0.385 \text{Sr}^{2+} \cdot 0.615 \text{Cr}^{3+} \cdot 0.985 \text{Cr}^{4+} \cdot 0.015 \text{O}_6$</td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>$\text{La}^{3+} \cdot 0.859 \text{Sr}^{2+} \cdot 0.141 \text{Cr}^{3+} \cdot 0.959 \text{Ru}^{4+} \cdot 0.041 \text{O}_6$</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>$\text{La}^{3+} \cdot 0.389 \text{Sr}^{2+} \cdot 0.611 \text{Cr}^{3+} \cdot 0.989 \text{Ru}^{4+} \cdot 0.011 \text{O}_6$</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>$\text{La}^{3+} \cdot 0.854 \text{Sr}^{2+} \cdot 0.146 \text{Cr}^{3+} \cdot 0.984 \text{Cr}^{4+} \cdot 0.024 \text{Ru}^{4+} \cdot 0.122 \text{O}_6$</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The substitution of divalent Sr for trivalent La requires charge compensation, which can be achieved by the formation of either tetravalent chromium or oxygen vacancies.

The partial substitution of divalent Sr for trivalent La in LaCrO$_3$ leads to the same decrease in unit cell volume despite the fact that Sr$^{2+}$ is a larger ion and has a lower valence state. A probably explanation of this lies in the formation of Cr$^{4+}$ (having a lower ionic radius than Cr$^{3+}$) which compensates for either steric and electronic effects of Sr$^{2+}$ doping. The formation of certain amount of oxygen vacancies, however, can not be excluded.

However, the progressive substitution of Cr$^{3+}$ for Ru$^{4+}$ (having almost the same ionic radius) in the B position of La$_{1-x}$Sr$_x$Cr$_{1-x}$O$_3$ phase simply decreases the need for Cr$^{4+}$ and causes an increase in the unit cell volume (Table II). As a result of the above effect, a decrease in the Ru content reduces the unit cell volume to the smallest value for $x = 0$. The further decrease of the unit cell volume observed in the sample with higher Sr content ($y = 0.25$) can be ascribed to the increase of Cr$^{4+}$ in the some proportion of the Sr$^{2+}$ content.

The O$_{1s}$ photoelectron spectra of the ruthenium catalysts (Fig. 5) indicate that at least two kinds of oxygen species are present on the surface. The lower binding energy of O$_{1s}$ (529.0–529.5 eV) is attributed to lattice oxygen. A shoulder around BE $= 530.5$ eV, clearly pronounced only for the sample with $x = 0.025$ could be assigned to the absorbed oxygen according to Seiyama.\textsuperscript{15}

Oxygen sorptive properties of La$_{1-x}$Sr$_x$Cr$_{1-x}$Ru$_x$O$_3$ (0 $\leq x \leq 0.100$) samples in relation to structural defects and the role of absorbed oxygen in the activity and kinetics of CO oxidation is the subject a separate study.

The stabilization of ruthenium ions by incorporating them in the perovskite structure enables the oxidation activity to be investigated with no significant loss of Ru.
Fig. 5. Photoelectron spectra of O_{1s} of La_{1-x}Sr_{x}Cr_{1.2}Ru_{0.8}O_{3} (0.025 ≤ x ≤ 0.100).

The effect of temperature on the rate of CO oxidation was studied on La_{1-x}Sr_{x}CrO_{3} and a series of ruthenium samples in the temperature range of 100 °C to 300 °C using a CO/O_{2} = 1 reaction gas mixture.

Fig. 6. Arrhenius plots of the global rate of CO oxidation on perovskite samples.
The specific surface area of all the synthesized samples was about 1 m²/g. Therefore, the global rate of CO oxidation per gram or referred to the BET surface area of the catalysts is practically the same.

The global CO oxidation rates and specific rates calculated per surface ruthenium atom (taken from Table I), in Arrhenius form, are plotted in Fig. 6 and Fig. 7, respectively. As can be seen from Fig. 6, even a small substitution of Ru⁴⁺ for Cr⁴⁺ in the La₁₋ₓSrₓCrO₃ matrix results in an enhanced oxidation rate and in an increase of the apparent activation energy from 56 kJ to 93 kJ. The strontium chromate phase, stable to the temperature of 1250 ºC¹³ under oxidative conditions, present in all samples in approximately the same amount, is not essential for the activity. The global CO oxidation rate increases with further progressive substitution of Ru⁴⁺ for Cr³⁺. However, the observed increase in the reacton rate does not follow the mole fraction of Ru (x) in the bulk of the samples. Almost the same global rate is obtained on the samples Ru₀₀.⁰⁷₅ and Ru₀₁.₀₀₀, with different degree of substitution of Ru in the bulk.

The XPS results (Table II) revealed not only higher Ru and Sr and lower Cr and La surface atomic concentrations in respect to those in the bulk, but also that samples Ru₀₀.⁰⁷₅ and Ru₀₁.₀₀₀ had very similar surface concentrations of ruthenium ions.

![Fig. 7. Arrhenius plots of the specific rate of CO oxidation on perovskite samples.](image)

These results indicated that surface Ru⁴⁺ ion have an essential influence on the overall activity. Moreover, samples with Ru mole fraction in the range 0.05 ≤ x ≤ 0.100 exhibits nearly the same oxidation rate per Ru surface atom (Fig. 7). Since no other oxidation states of Ru were detected on the surface layers, the oxidation activity could be attributed to the Ru⁴⁺ ion.

The identical apparent activation energy \( E = 93 \text{ kJ/mol} \) obtained on samples with a ruthenium content in the range 0.05 ≤ x ≤ 0.100 and the very similar rate per ruthenium surface ion suggest that all the Ru sites are exposed and that mainly these
seats participate in the reaction. In accordance with the previous, it can be considered that no significant segregation of ruthenium on the surface occurs and that matrix effects arise from the fact that perovskite permits the high dispersion of Ru\(^{4+}\).

It is interesting to realize the important difference in the specific activity of the sample with the lowest ruthenium content (\(x = 0.025\)). The significantly lower activity per ruthenium ion implies that not every exposed Ru\(^{4+}\) ions is active in CO oxidation. Since, the same apparent activation energy was obtained for this sample as for the samples with higher ruthenium contents, one of the possible explanations of this difference in activity could be found in the distance of the Ru ions in the perovskite phase. However, further work is necessary to clarify this point.

CONCLUSION REMARKS

The investigated catalysts, with the general formula La\(_{1-x}\)Sr\(_x\)Cr\(_2\)Ru\(_3\)O\(_{12}\) (0 \(\leq x \leq 0.100\)), achieved a perovskite phase with about 20% of SrCrO\(_4\). The amounts of metals, determined by XPS analysis of samples calcinated in air at 1000 °C, correspond to the stoichiometric values of the proposed chemical compositions. This proves that the incorporation of Ru into a perovskite matrix prevents the oxidation of ruthenium into volatile polyvalent oxides and their consequential escape from the samples up to 100 °C.

XPS data indicate a surface enrichment in Ru and Sr. It can, furthermore, be concluded that an increase in the global rate reflects the surface enrichment in Ru. The invariance of the apparent activation energy and the specific rate, computed per ruthenium surface atom in the samples, with a ruthenium content in the range 0.050 \(\leq x \leq 0.100\), suggest the Ru\(^{4+}\) ions are exposed and that they play a dominant role in the reaction.

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фазе присутан и манифеста \( \text{SrCrO}_3 \)фазе. Концентрације \( \text{Sr} \) и \( \text{Ru} \) површинских масовима, израчунате из X-фотоселективних спектроскопија, су веће у односу на њихову концен-
трацију у маси. Енергија везе \( \text{Ru}_p \) је иста за све узорке и карактеристична је за \( \text{Ru}^{4+} \). Кинетика оксидације угљеномоноксида испитана је у диференцијалном рециркулаци-
оном реактору. Резултати показују дадени мача замена \( \text{Cr}^{3+} \) на \( \text{Ru}^{4+} \) у \( \text{La}_1.5\text{Sr}_2\text{CrO}_3 \) доводи до значљивог пораста активности и енергије актинације. Укупна брзина оксидација СО,
обручанта по јединици специфичне површине, је скоро пропорционална порасту атомск-
ске концентрације \( \text{Ru}^{4+} \) на површини узорка, односно \( \text{Ru}^{4+} \) обновљен је иста привидна
енергија актинације од \( E = 93 \text{ kJ/mol} \) и иста специфична брзина оксидације по површинс-
ском јону \( \text{Ru}^{4+} \), што указује на то да су јои \( \text{Ru}^{4+} \) изложени и да они преходом учествују
у реакцији.

(Примећено 6. јул 1999.)

REFERENCES