Partial oxidation of methane to synthesis gas over Rh - promoted perovskites

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1. Background and motivation

*Partial oxidation of methane to syngas:*

**Reaction concept**

\[
\begin{align*}
\text{CH}_4 + \text{MO}_x & \rightarrow \text{CO} + 2\text{H}_2 + \text{MO}_{x-1} \\
\text{MO}_{x-1} + 0.5\text{O}_2 & \rightarrow \text{MO}_x
\end{align*}
\]

Possible by-product formation:

\[
\begin{align*}
\text{CH}_4 + 2\text{MO}_x & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{MO}_{x-1} \\
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2
\end{align*}
\]
2. Perovskites

**ABO$_3$**

**Doping strategy**

$\text{La}^{\text{III}}\text{Fe}^{\text{III}}\text{O}_3 \rightarrow \text{La}_{0.75}\text{Sr}_{0.25}(\text{Fe}_{0.8}\text{Co}_{0.2})_{1-x}\text{Ga}_x\text{O}_{3-\delta}$

- **B-site doping** with $p$- $(\text{Ga}^{3+})$ and $d$-cations $(\text{Co}^{3+}/\text{Co}^{2+}, \text{Fe}^{3+}/\text{Fe}^{2+})$ to adjust the number of oxygen vacancies

- **A-site doping** with two-valent cations $(\text{Sr}^{2+})$ to create oxygen vacancies $(\delta)$

Rh is added to enhance catalytic properties
3. X-ray diffraction studies

Orthorhombic perovskite phase

La$_{0.75}$Sr$_{0.25}$(Fe$_{0.8}$Co$_{0.2}$)$_{1-x}$Ga$_x$O$_{3-\delta}$

Ga - 0.1  La$_{0.75}$Sr$_{0.25}$Fe$_{0.7}$Co$_{0.2}$Ga$_{0.1}$O$_{3-\delta}$
Ga - 0.25 La$_{0.75}$Sr$_{0.25}$Fe$_{0.6}$Co$_{0.15}$Ga$_{0.25}$O$_{3-\delta}$
Ga - 0.4  La$_{0.75}$Sr$_{0.25}$Fe$_{0.5}$Co$_{0.1}$Ga$_{0.4}$O$_{3-\delta}$
Ga - 0.6  La$_{0.75}$Sr$_{0.25}$Fe$_{0.3}$Co$_{0.1}$Ga$_{0.6}$O$_{3-\delta}$

Impurities in Ga-0.6 sample belong to SrLaGa$_3$O$_7$ phase
3. X-ray diffraction studies

Rietveld refinement

Lattice parameters increase with gallium concentration since Ga$^{3+}$ has a larger ionic radius compared to Co$^{3+}$ and Fe$^{3+}$.
Experimental Setup

Source: F. Mudu, PhD thesis
Transient Catalytic Test (CH$_4$/O$_2$)

CH$_4$ conversion % = 100x \( \frac{p(\text{CH}_4)_{\text{in}} - p(\text{CH}_4)_{\text{out}}}{p(\text{CH}_4)_{\text{in}}} \)

CO selectivity % = 100x \( \frac{p(\text{CO})_{\text{out}}}{p(\text{CO})_{\text{out}} + p(\text{CO}_2)_{\text{out}}} \)

Typical MS raw data output from a pulse test.
Methane conversion of Rh promoted perovskites at 873K

![Graph showing methane conversion over different Rh/Ga ratios](image)

- Rh/Ga10
- Rh/Ga25
- Rh/Ga40
- Rh/Ga60

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CO selectivity of Rh promoted perovskites at 873K

![Graph showing CO selectivity versus pulse of CH₄ for different Rh/Ga compositions.](image-url)
La$_{0.75}$Sr$_{0.25}$Fe$_{0.6}$Co$_{0.15}$Ga$_{0.25}$O$_{3-\delta}$

(+ 0.5 wt% Rh)

Distribution of CO, CO2, CH4

CH4 conversion

CO selectivity

Content of Ga

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XPS of Ga modified perovskites

La$_{0.75}$Sr$_{0.25}$Ga$_{0.4}$Fe$_{0.5}$Co$_{0.1}$O$_{(3-\delta)}$ (reduced)

O1s

531.3 eV (42 %)  
528.8 eV (O$^{2-}$) (58 %)

531.3 eV (49 %)  
528.6 eV (O$^{2-}$) (51 %)

La$_{0.75}$Sr$_{0.25}$Ga$_{0.4}$Fe$_{0.7}$Co$_{0.2}$O$_{(3-\delta)}$ (as prepared)

Sr3d

133.9 eV

132.2 eV

Binding energy (eV)
HRTEM of Rh promoted perovskite oxides
Conclusions

- The synthesized samples were single perovskite phase materials, with a small amount of secondary LaSrGa$_3$O$_7$ phase in sample with 60 % gallium only.

- The catalytic tests of Rh promoted perovskites show that the total CO production decreases with the addition of Ga. The increase in CH$_4$ conversion with Ga addition is due to the steep increase in carbon deposit production. This can be related to the lower oxidation state reached by Co.

- The catalytic tests showed that Rh promoted Ga modified perovskites catalysts exhibit a more rapid deactivation with increasing amount of gallium. The deactivation of the catalysts involves both carbon deposits and less reduction of the active phase.

- X-ray photoelectron spectroscopy and Transmission electron microscopy studies have been performed on the surface of the Rh promoted perovskites. The Rh$_2$O$_3$ thin overlayer causes the surface to be enriched in Rh. Introduction of Ga into perovskites structure changes the Co/Fe ratio on the surface.
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Thank you for your attention