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

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1. Background and motivation

Methane ⟶ ***Syngas ($CO+H_2$)*** ⟶ ***Methanol***

Partial oxidation of methane to syngas:

Reaction concept

$$CH_4 + MO_x \rightarrow CO + 2H_2 + MO_{x-1}$$
$$MO_{x-1} + 0.5O_2 \rightarrow MO_x$$

Possible by-product formation:

$$CH_4 + 2MO_x \rightarrow CO_2 + 2H_2O + 2MO_{x-1}$$
$$CH_4 \rightarrow C + 2H_2$$

2. Perovskites ABO_3

Doping strategy

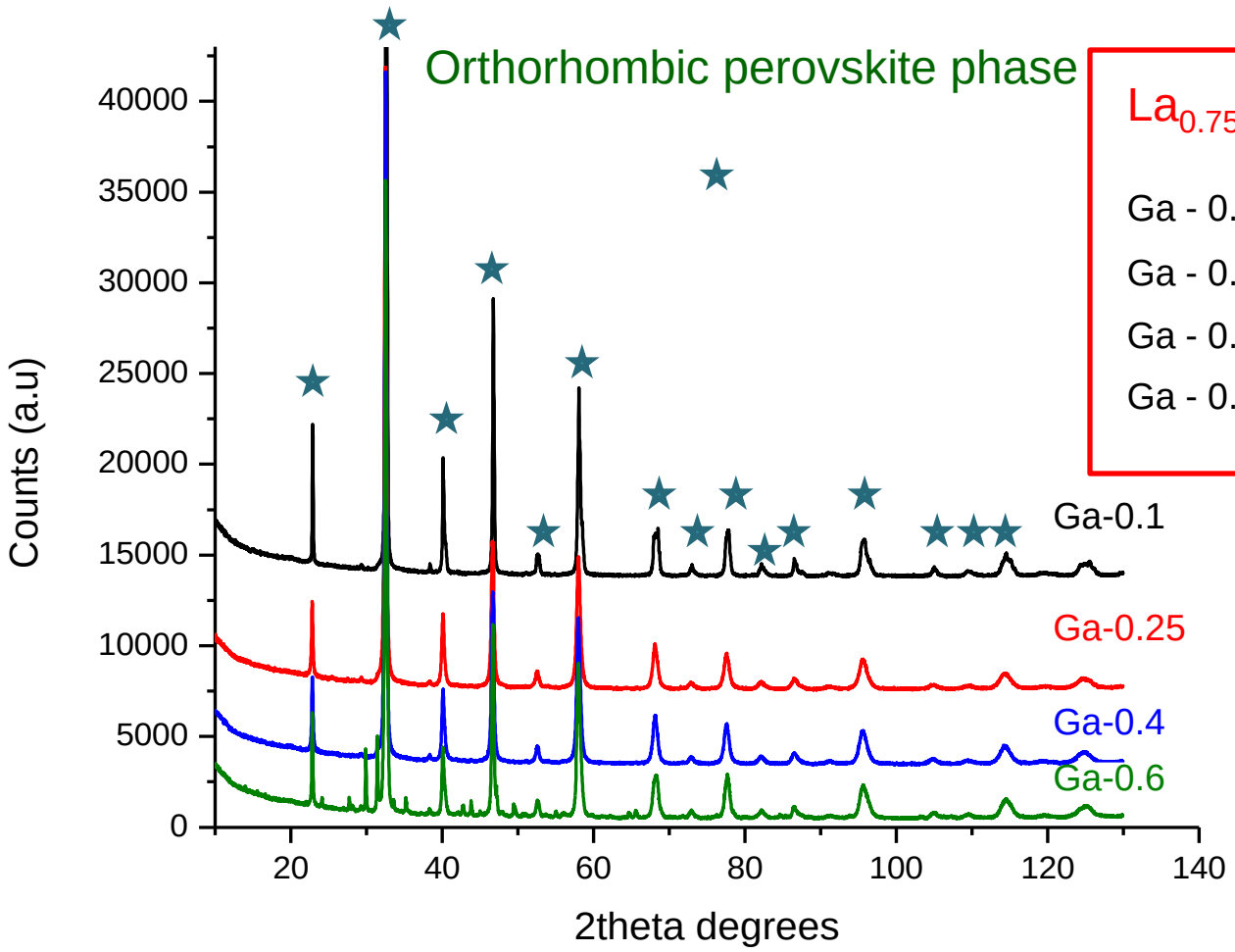
$La^{III}Fe^{III}O_3 \longrightarrow La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$

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

A-site doping with two-valent cations (Sr^{2+}) to create oxygen vacancies (δ)

Rh is added to enhance catalytic properties

3. X-ray diffraction studies



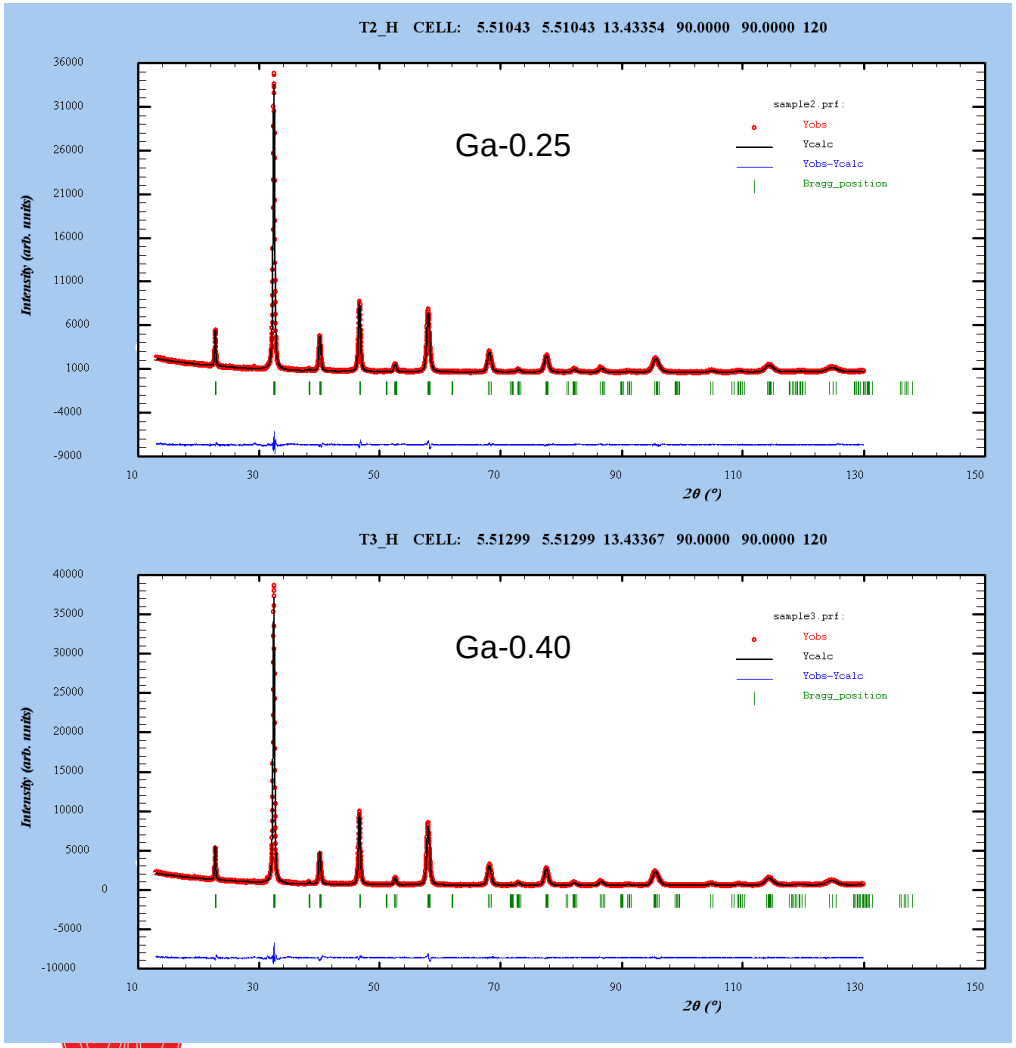
$La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$

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 $SrLaGa_3O_7$ phase

3. X-ray diffraction studies

Rietveld refinement

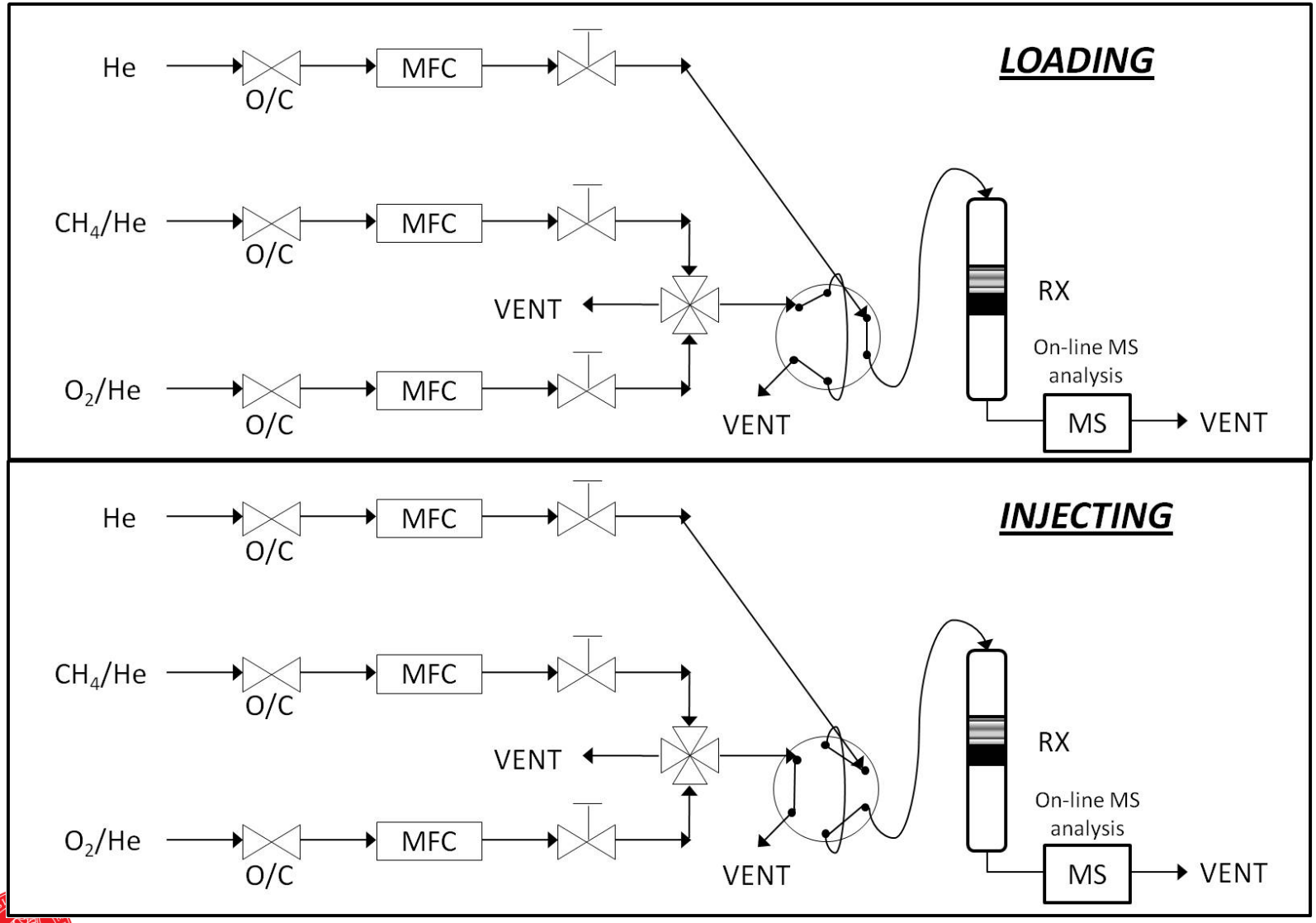


Lattice parameters

Sample	a	c
Ga-0.10	5.51042	13.39237
Ga-0.25	5.51043	13.43354
Ga-0.40	5.51299	13.43367
Ga-0.60	5.51494	13.36060

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

Experimental Setup

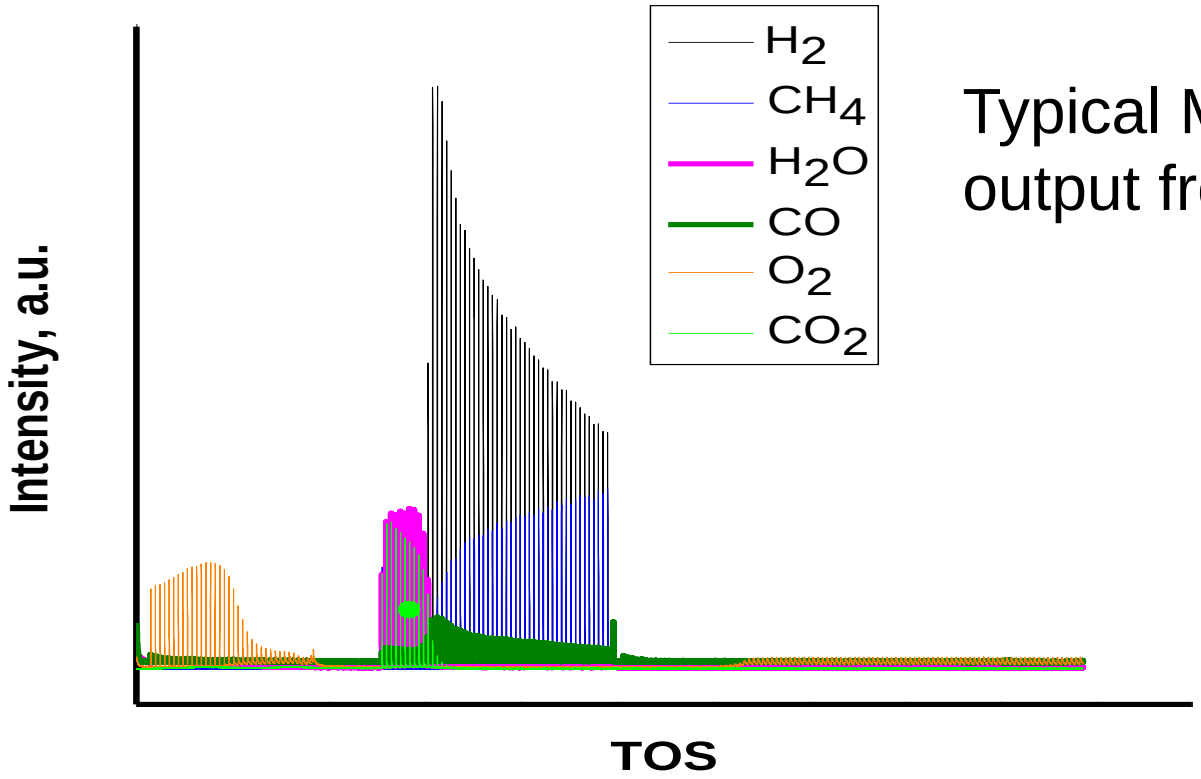


Source: F. Mudu, PhD thesis

Transient Catalytic Test (CH_4/O_2)

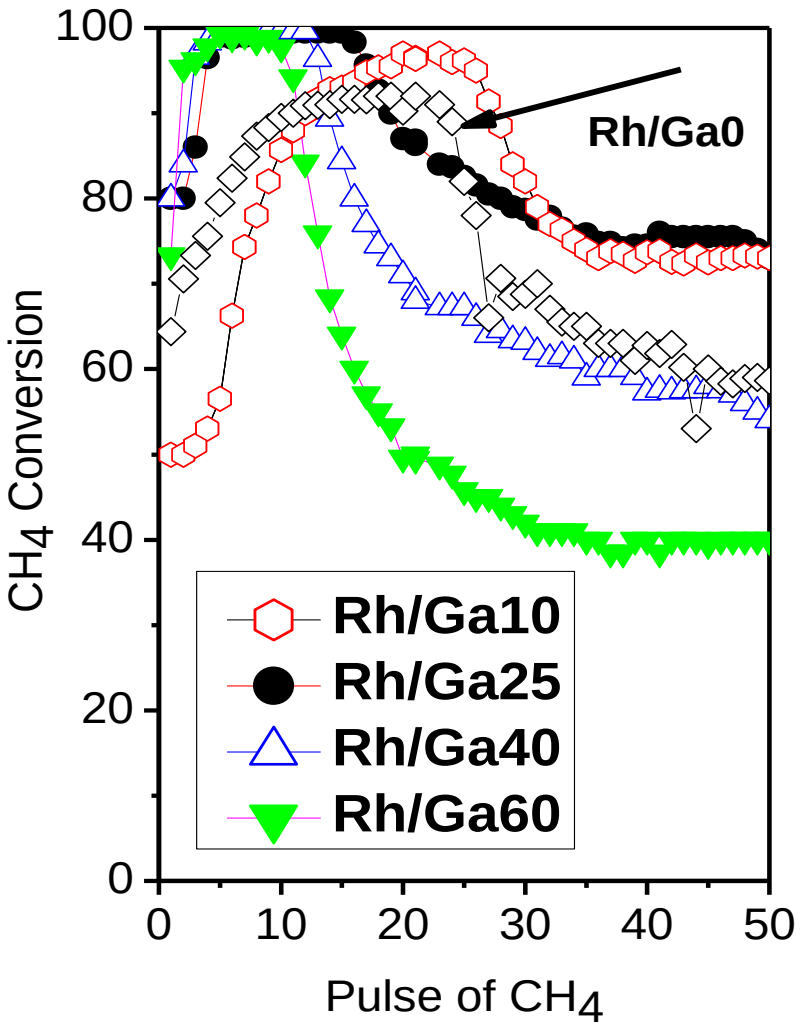
CH_4 conversion % = 100x ($p(CH_4)_{in}$ - $p(CH_4)_{out}$) / $p(CH_4)_{in}$

CO selectivity % = 100x $p(CO)_{out}$ / $p(CO)_{out}$ + $p(CO_2)_{out}$

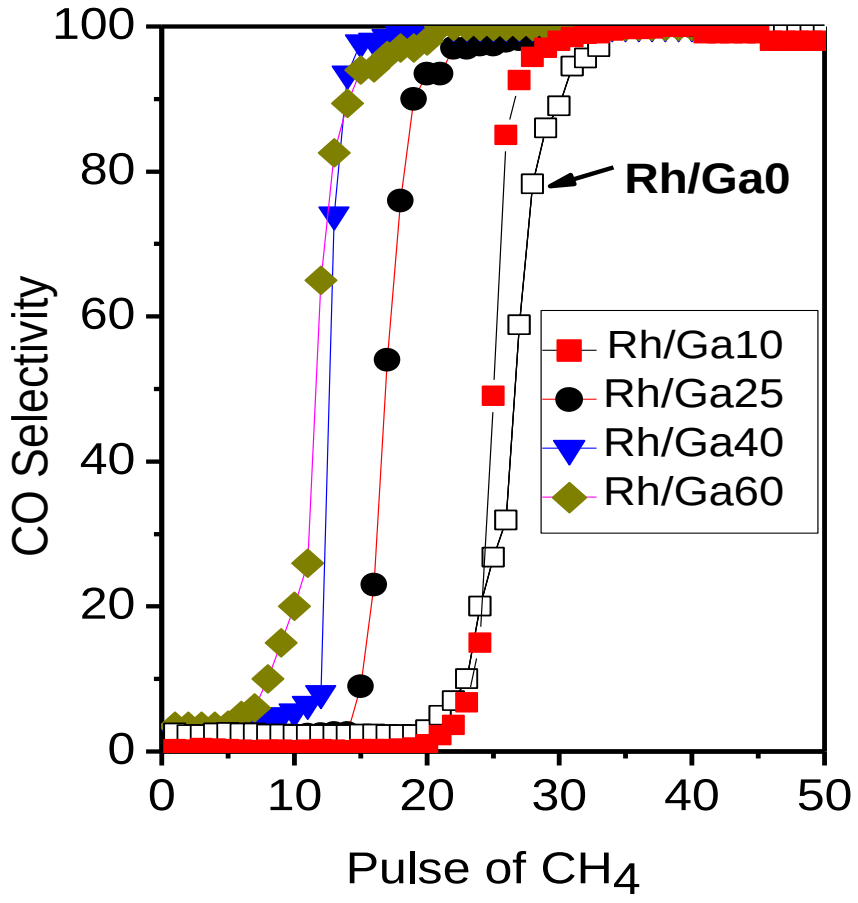


Typical MS raw data output from a pulse test

Methane conversion of Rh promoted perovskites at 873K

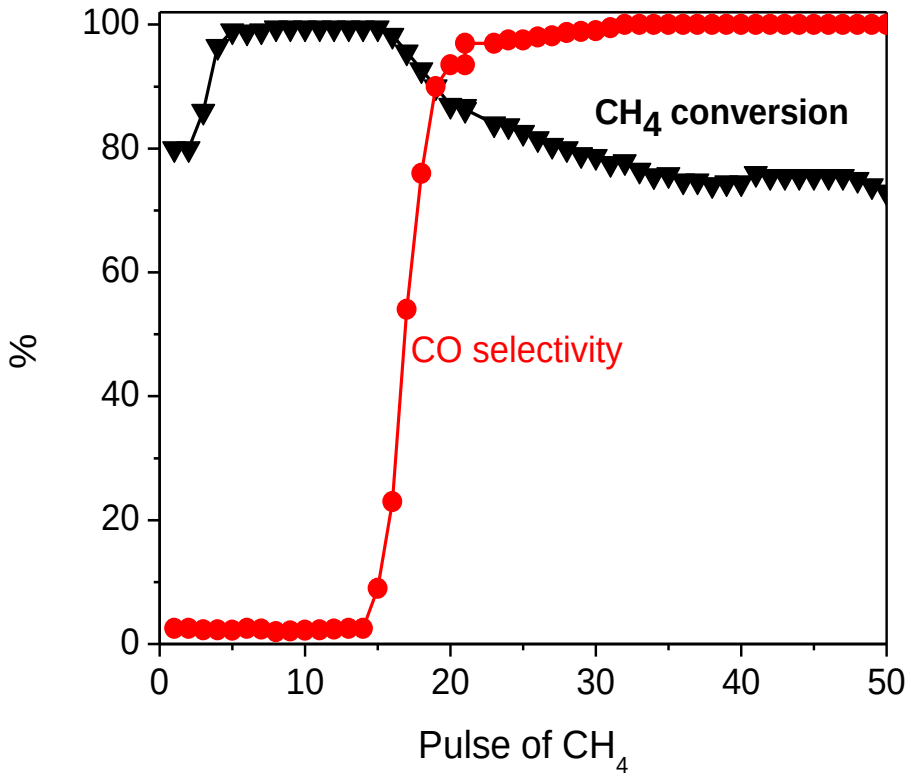


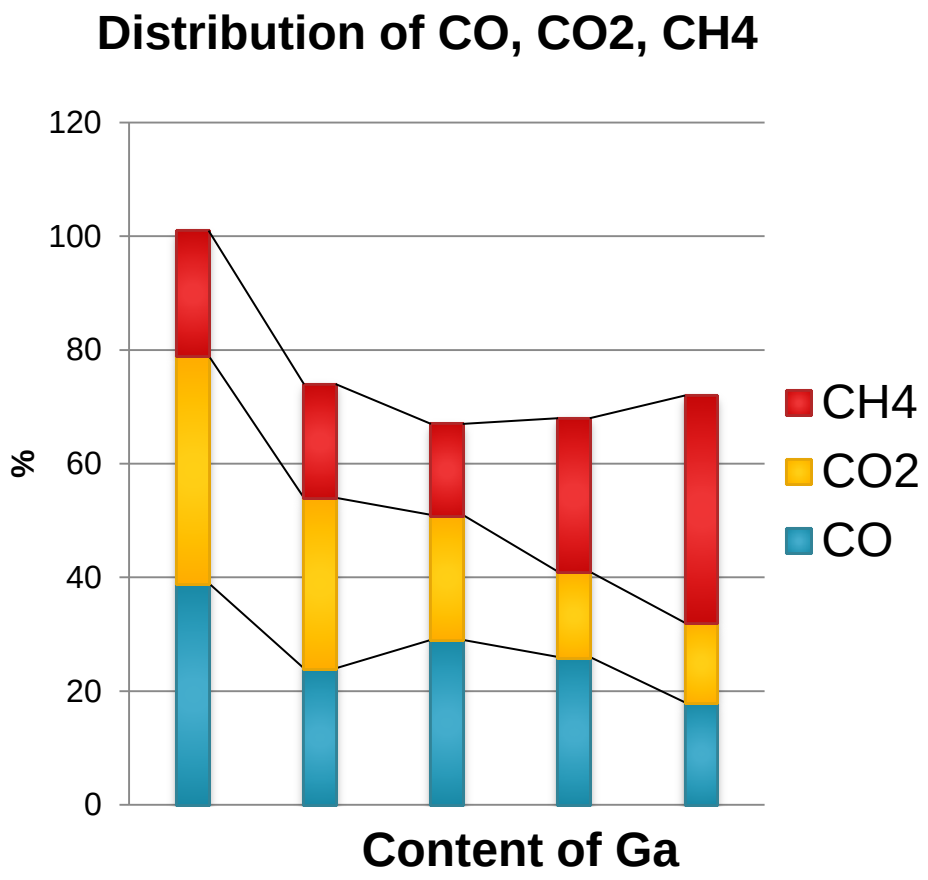
CO selectivity of Rh promoted perovskites at 873K



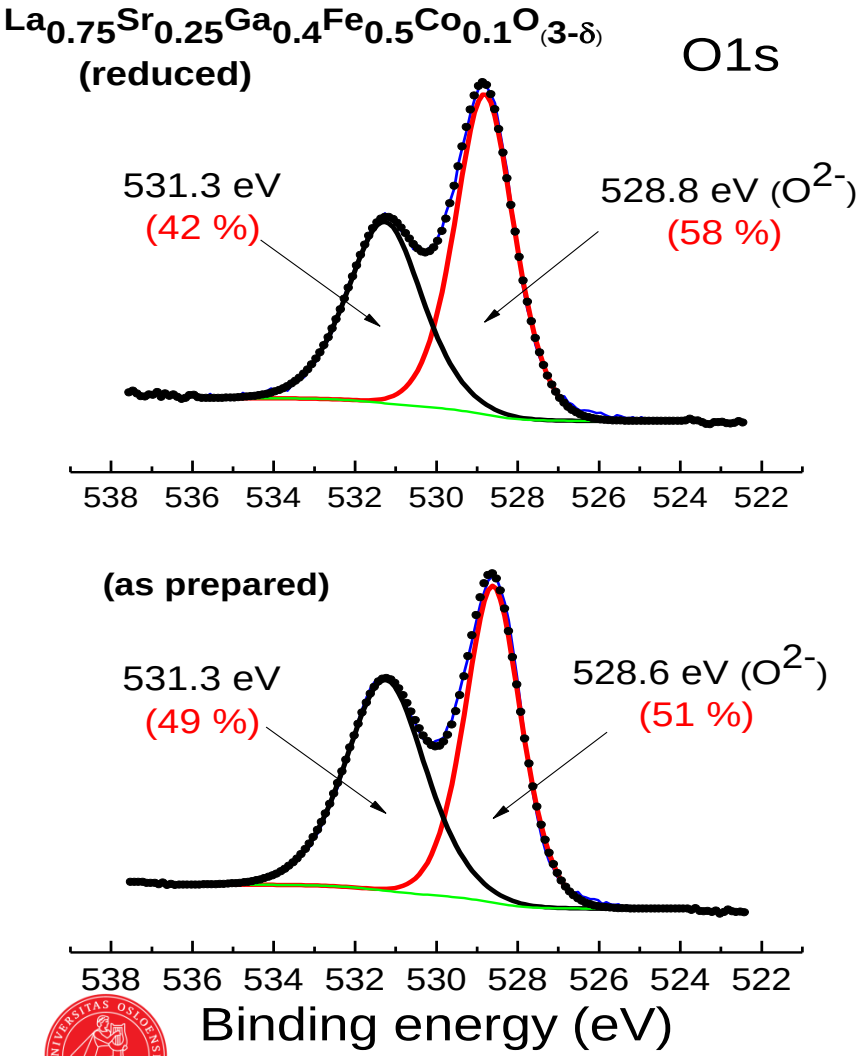
$La_{0.75}Sr_{0.25}Fe_{0.6}Co_{0.15}Ga_{0.25}O_{3-\delta}$

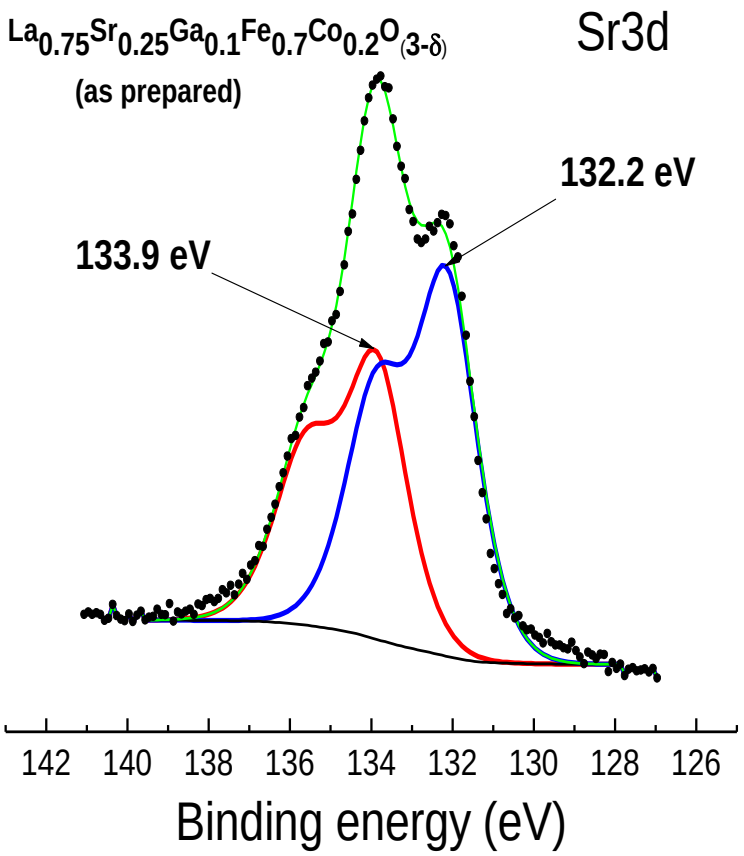
(+ 0.5 wt% Rh)



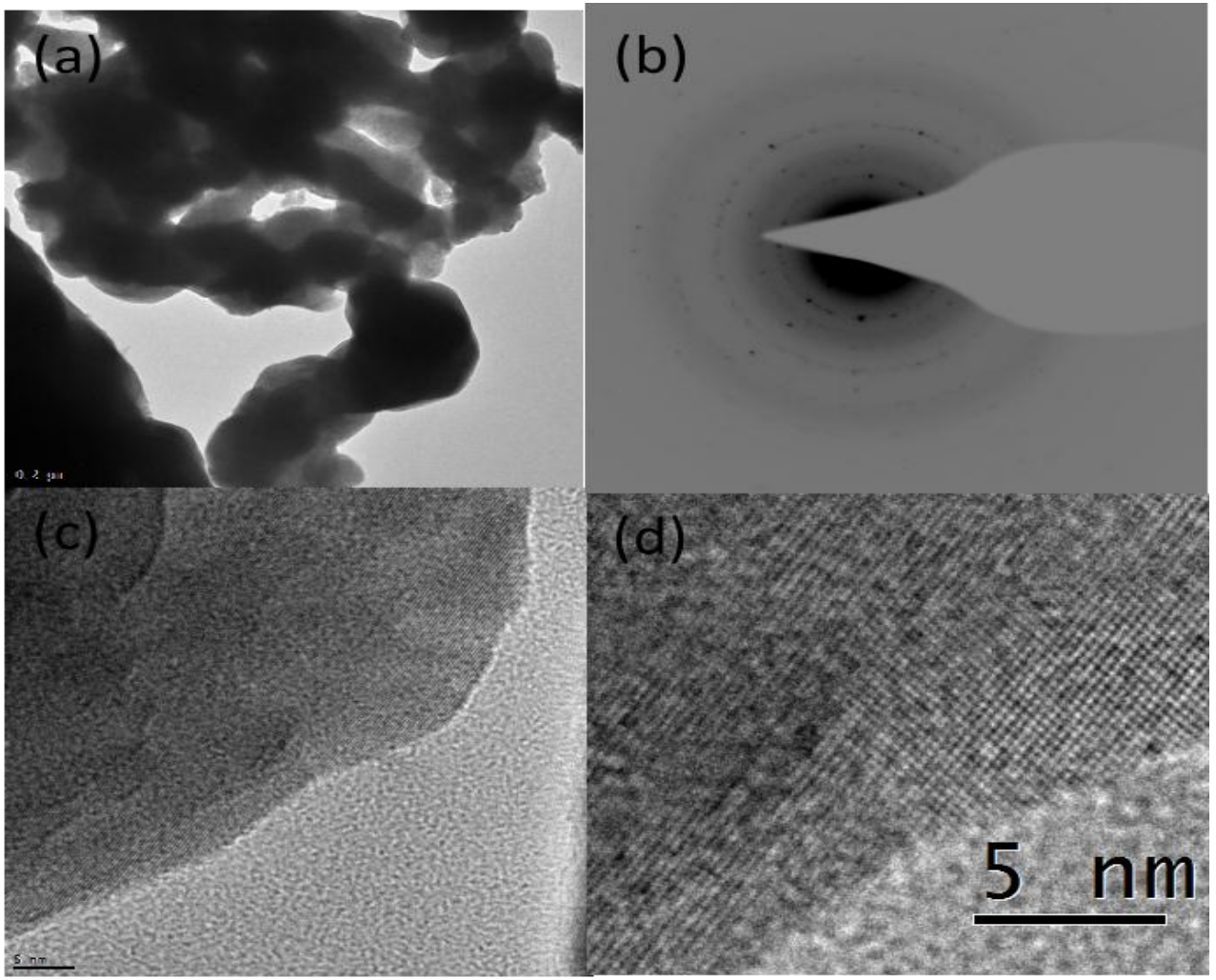


XPS of Ga modified perovskites





HRTEM of Rh promoted perovskite oxides



Conclusions

- The synthesized samples were single perovskite phase materials, with a small amount of secondary $LaSrGa_3O_7$ 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_2O_3 thin overlayer causes the surface to be enriched in Rh. Introduction of Ga into perovskites structure cnahges the Co/Fe ratio on the surface.

Acknowledgements

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Thank you for your attention