Ln/Fe-doped Sr_2TiO_4 Layered Perovskites: Effect of synthesis method and composition on physical-chemical and catalytic properties in oxidative coupling of methane

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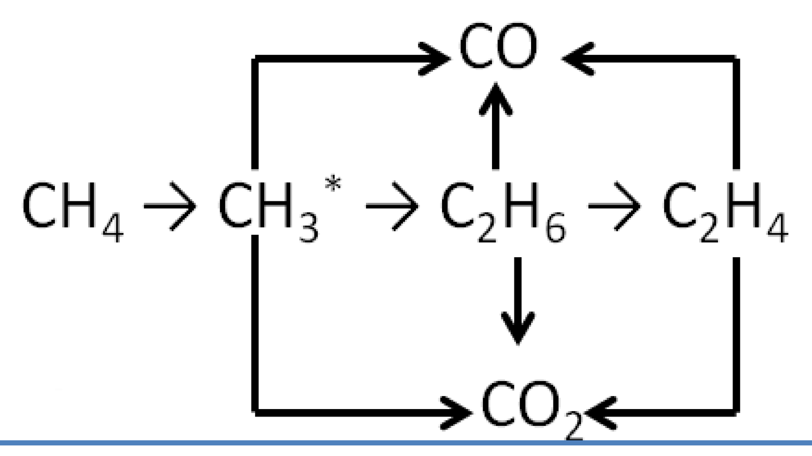
Introduction. Oxidative coupling of methane (OCM) – a potential direct route to produce C_2 hydrocarbons

$$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$$
$$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2$$

OCM simplified scheme

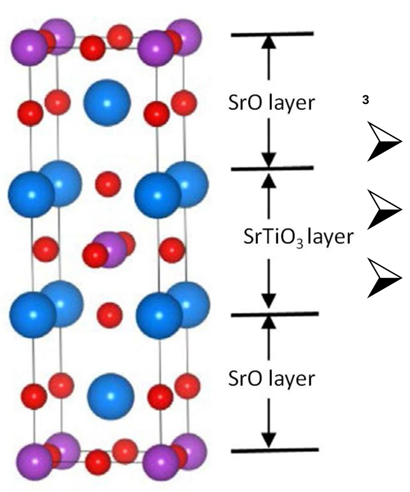


Heterogeneous-homogeneous reacion

- Activation of CH_4 in CH_3^* over active oxygen on the catalyst surface
- CH_3^* coupling in the gas phase→C_2H_6
- C_2H_6 oxidative dehydrogenation to ethylene on the catalyst surface centers

Nonselective oxidation of CH_4 in CO_x decreases the yield of C_2-hydrocarbons → the desing of new active and selective catalysts is the actual problem

Introduction. Layered strontium titanates – perspective catalysts for OCM



Sr_2TiO_4 structure:

- consists of $SrTiO_3$ and SrO alternating layers
- highly thermal and chemical stable
- flexible structure → substitution of Sr or/and Ti positions → tuning concentration of surface defects, active oxygen species → tailoring the OCM catalyst activity

The aim: **To study the impact of the cations nature partially replacing Sr (La, Nd, Pr) or Ti (Fe) and the method of their introduction in Sr_2TiO_4 on the morphologi-cal, structural, redox properties and OCM**

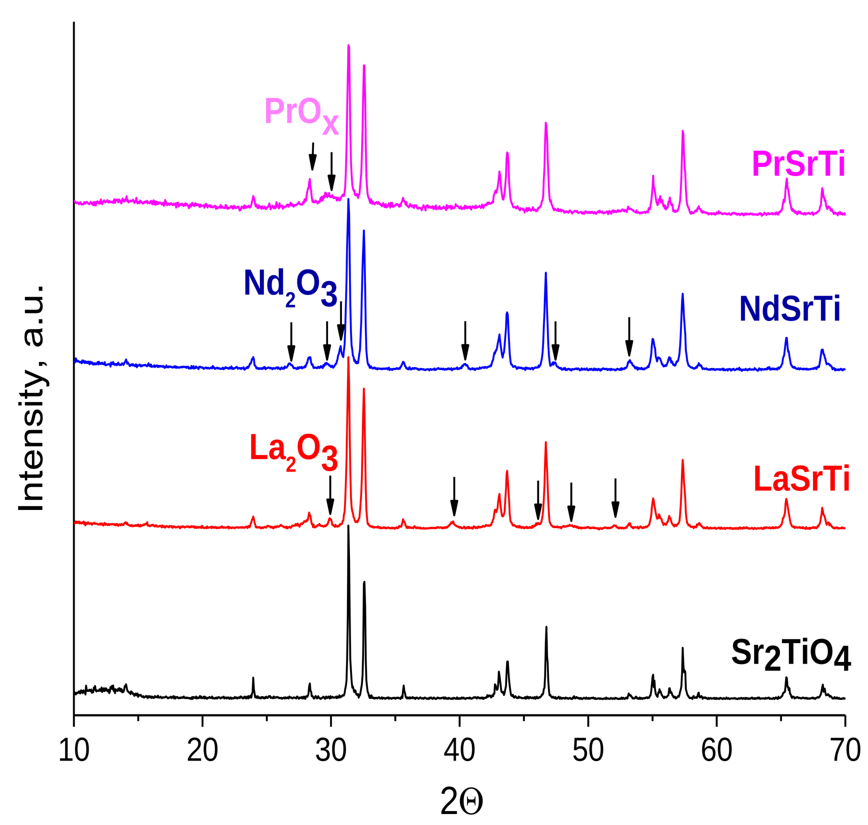
Samples and Synthesis

5% Ln/Sr_2TiO_4 (Ln= La, Pr, Nd) → **Sr_2TiO_4 impregnation by La, Pr,Nd nitrates**

$Ln_xSr_{2-x}TiO_4$ (Ln= La, Pr, Nd, x= 0, 0,1)
$Sr_2Fe_yTi_{1-y}O_4$ (y=0-0.3) → **Sol-gel using polimeric precursors**

Phase composition

5% Ln/Sr_2TiO_4 (impregnation)

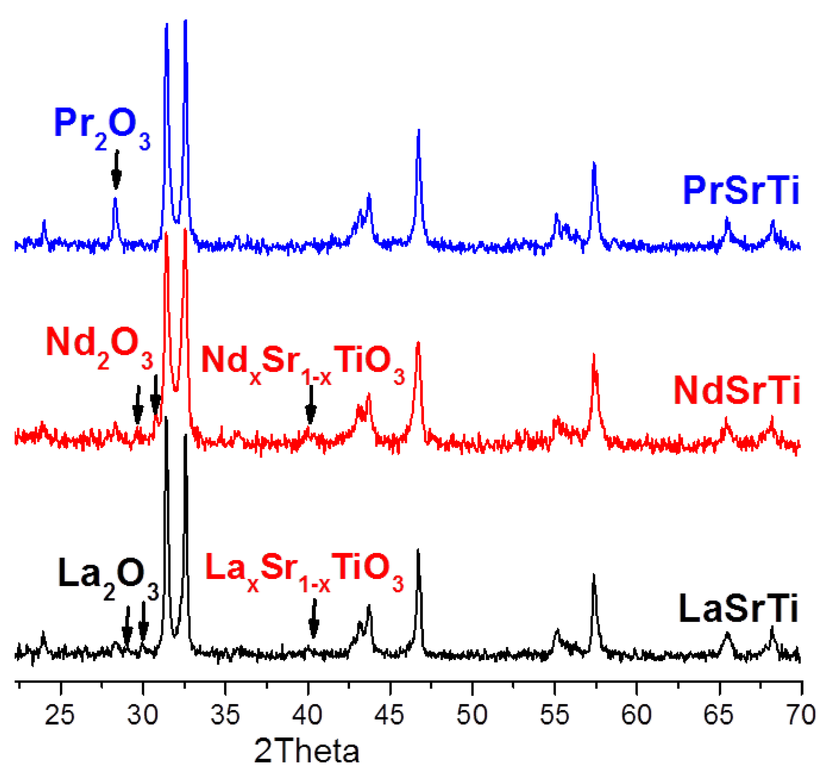


- all samples contain *Ln oxides*
- *Ln* are not embedded in *Sr_2TiO_4*

$Sr_2Ti_{1-y}Fe_yO_4$ (y=0-0.3) (sol-gel)

- all samples are single phase layered perovskites
- changed lattice paramerers evidence Fe incorporation into strontium titanate structure

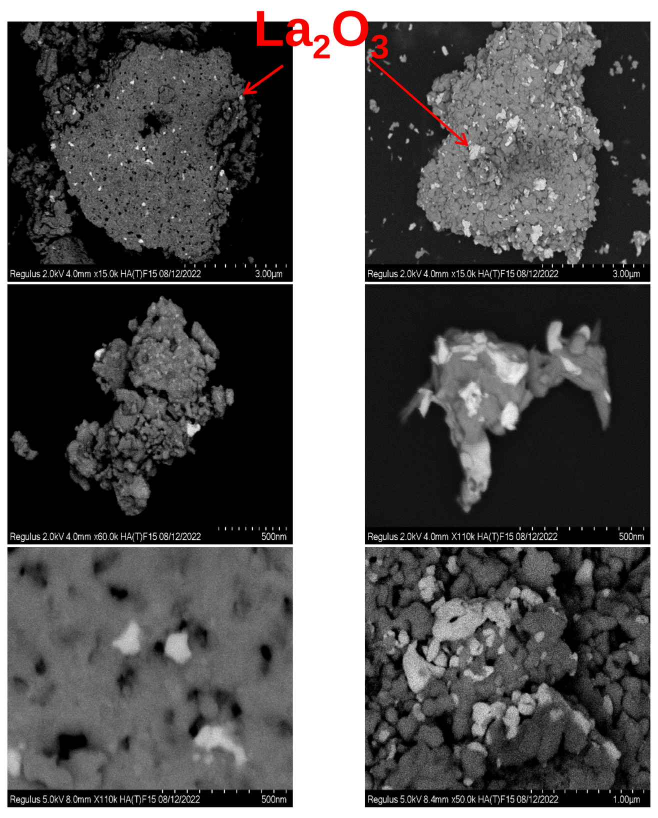
$Sr_{1.9}Ln_{0.1}TiO_4$ (sol-gel)



- **multiphase, Ln nature influences phase composition**
- ***La, Nd*: formation intermediate *$Ln_xSr_{1-x}TiO_3$***
- ***Pr^{3+}*: formed only layered *$Sr_{x+1}Ti_xO_{3x+1}$***
- ***Ln^{3+}* partially incoporate in perovskite high dispersion of Ln oxides**

Morphology (Field Emission Scanning Electron Microscope (FE-SEM))

$La_{0.1}Sr_{1.9}TiO_4$ (sol-gel) | **5%La/Sr_2TiO_4 (impregnation)**

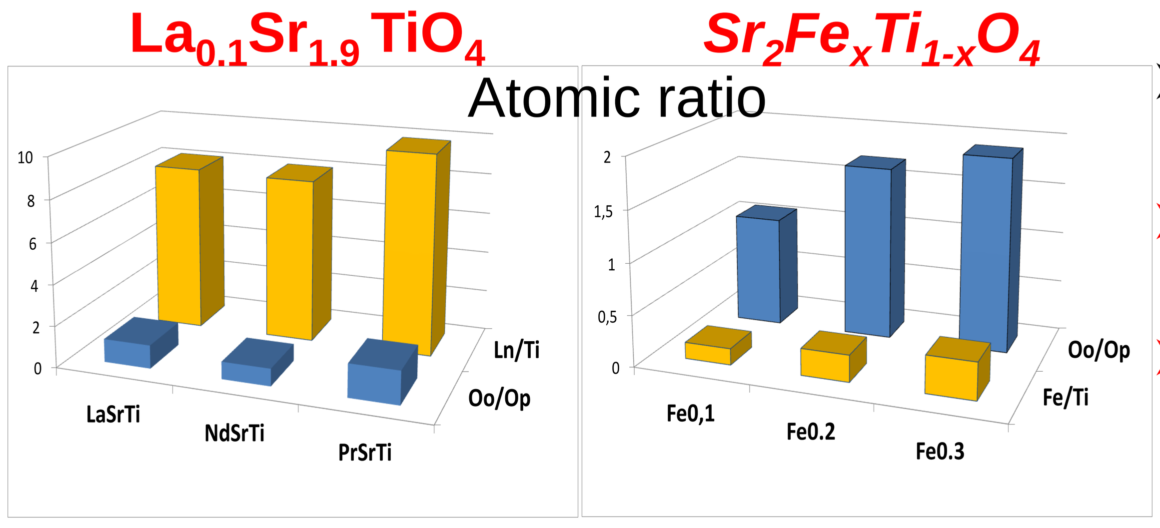


- **$La_{0.1}Sr_{1.9}TiO_4$: *La_2O_3* particles upto 200 nm**
- **5%La/Sr_2TiO_4: *La_2O_3* particles upto 300 nm and agglomerates upto 1μ**

Sol-gel method provide high Ln oxide dispersion

Surface composition (X-Ray Photoelectron Spectroscopy)

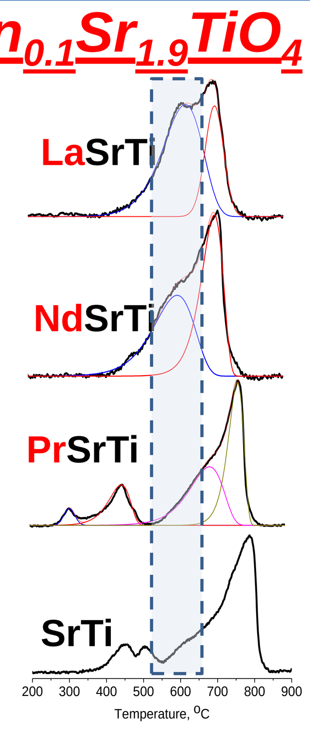
$La_{0.1}Sr_{1.9}TiO_4$ | ***$Sr_2Fe_xTi_{1-x}O_4$***



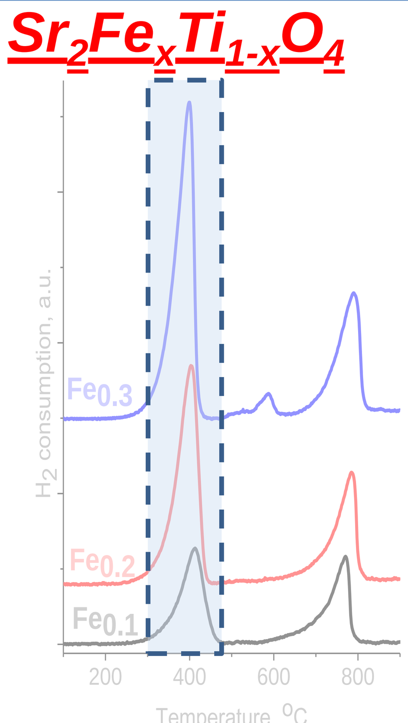
- Surface is *enriched* by *Ln or Fe*
- *Ln* affects *oxygen forms ratio*
- *Ratio O_o/O_p* (oxide/ perovskite) *rises at in-creasing Fe concentra-tion*

H_2-Temperature Programmed Reduction

$Ln_{0.1}Sr_{1.9}TiO_4$



$Sr_2Fe_xTi_{1-x}O_4$

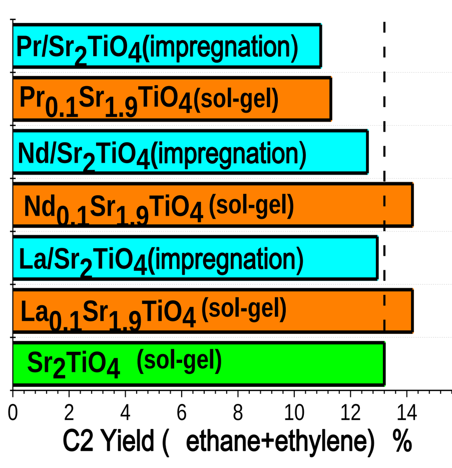


- ***Three temperature region of oxygen forms reduction:*** **300-500°C –weakly bound oxygen; 500-650°C and 650-850°C – surface and bulk oxygen**
- **La(Nd)SrTi → mainly surface lattice oxygen and bulk oxygen**
- **PrSrTi and SrTiFe→ large amount of weakly bound oxygen reduced at 300-500°C**

Catalysts activity in Oxidative Coupling of Methane

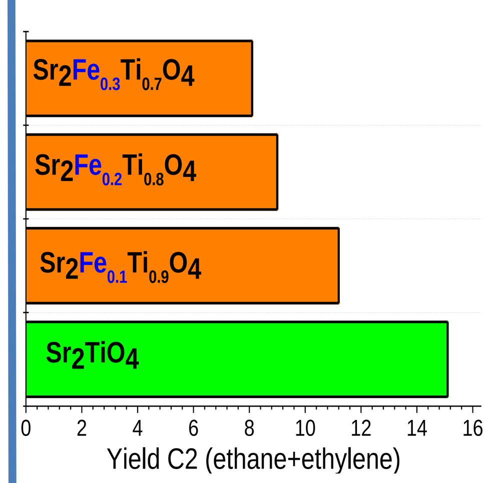
Testing: *45% CH_4 in air(CH_4: O_2 ~4); GHSV - 75000 h^{-1}; 850-900°C*

Ln-Sr_2TiO_4



- **La and Nd doped sol-gel samples are the most active due to the presence of surface lattice oxygen promotes C_2 forming and high oxides dispersion**

$Sr_2Ti_{1-y}Fe_yO_4$



- ***Fe doping leads to lowering the activity due to large amount appearance of weakly bound oxygen favoring CO_x formation***

Conlusion

- **Higher yield of C2 over La and Nd-doped sol-gel samples links with high oxides dispersion and the presence of oxygen forms having optimal bound energy.**
- **Decreasing yield of C2 in the case of Fe and Pr-doped samples is due to weakly bound oxygen forms facilitating CO_x formation.**