ACTIVITY, STABILITY AND LIMIT CYCLES BEHAVIOR OF CO OXIDATION OVER Ir/$La_{1-x}Sr_xMnO_3$-PEROVSKITE CATALYSTS

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1. Introduction

- **Perovskites** (ABO_3, where A: a lanthanide and B: a transition metal, e.g., Mn^{3+}, Cr^{3+}, V^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}), are characterized by remarkable thermal stability, oxygen ion mobility and crystalline structure. Good catalytic activity in oxidation reactions e.g., CO oxidation, but at elevated temperatures
- **Iridium** is a relatively inexpensive noble metal with exceptional properties in CO and hydrocarbon oxidation, NOx reduction reactions.

Sintering & deactivation of Ir-based catalysts, under high temperatures & oxidizing conditions

Stabilization of Ir nanoparticles by using supports with high oxygen storage capacity / lability values (Fig. 1)

Objectives

- Synthesis of $La_{1-x}Sr_xMnO_3$ perovskites and usage as supports, with high OSC values, for the dispersion of Ir nanoparticles.
- Characterization of LSM supports & Ir-LSM catalysts by various techniques.
- Evaluation of Ir-LSM catalysts' catalytic activity and stability on CO oxidation.
- Understanding of structure-activity-stability correlations of Ir-LSM catalysts .

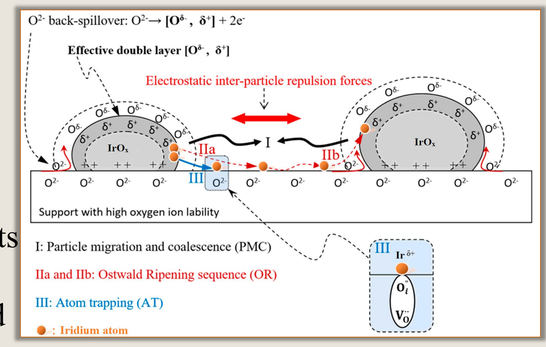

Fig. 1 Model for sintering resistance against particle migration & coalescence (PMC) or Ostwald Ripening sequence (OR) and redispersion induced by the simultaneous action of interparticle repulsion forces arising from effective double layer and atom trapping at oxygen ion vacancies. Modified picture from Goula et al., *Catalysts*, 2019, 9(6), 541.

2. Experimental

2.1 Ir-LSM catalysts synthesis

- ✓ Preparation of Perovskites $La_{1-x}Sr_xMnO_3$ via co-precipitation (**Table 1**)
- ✓ Ir addition on LSM by wet impregnation.

2.2 Characterization techniques

- ✓ N_2 physical adsorption-desorption isotherms (BET-BJH)
- ✓ X-ray powder diffraction (XRD) analysis
- ✓ Hydrogen temperature programmed reduction (H_2-TPR)
- ✓ Isothermal hydrogen chemisorption (H_2-Chem)

2.3 Kinetic and stability experiments

Kinetic experiments in a quartz fixed-bed reactor,
Feed Gas mixture: 1 % v/v CO, 5 %v/v O_2 /He, F_T=160 mL/min (wGHSV=480 000 mL/g_{cat}h)

- ✓Pre-reduced Ir-catalysts (25% H_2/He, 400° C, 1 h)
- ✓Pre-oxidized Ir-catalysts (20% O_2 /He, 400° C, 1 h)
- ✓Thermal stability experiments at 350°C after consecutive oxidation steps at 600°C and 750°C.

Table 1. Textural, morphological and reducibility characteristics of the $La_{1-x}Sr_xMnO_3$ perovskite supports and the counterpart 2wt%Ir/$La_{1-x}Sr_xMnO_3$ catalysts.

Sample code	Chemical Formula	S_{BET} (m^2/g)	Average pore diameter (nm)	OSC (μmol O_2/g)	Mean Ir particle size (nm)*	Ir Dispersion (%)
LSM00	$LaMnO_3$	12.0	10.9	671	-	-
LSM30	$La_{0.7}Sr_{0.3}MnO_3$	10.4	9.84	766	-	-
LSM50	$La_{0.5}Sr_{0.5}MnO_3$	6.8	8.91	886	-	-
LSM70	$La_{0.3}Sr_{0.7}MnO_3$	11.3	8.79	1219	-	-
Ir/LSM00	2wt%Ir/$LaMnO_3$	9.7	11.9	502	1.1	63
Ir/LSM30	2wt%Ir/$La_{0.7}Sr_{0.3}MnO_3$	10.5	9.96	981	1.1	62
Ir/LSM50	2wt%Ir/$La_{0.5}Sr_{0.5}MnO_3$	6.2	8.11	1203	1.0	73
Ir/LSM70	2wt%Ir/$La_{0.3}Sr_{0.7}MnO_3$	11.0	13.7	1348	1.2	61

3. Results

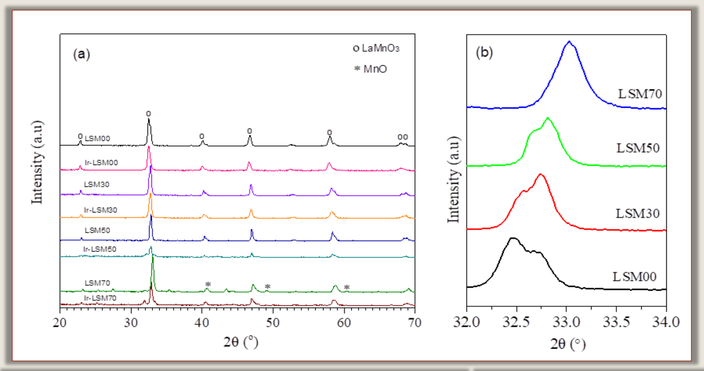

Figure 1. X-ray diffractions patterns of LSM supports and Ir/LSM catalysts at 20° < 2θ < 70° (a). Enlarged XRD patterns at 32°<2θ<34° for LSM perovskites (b).

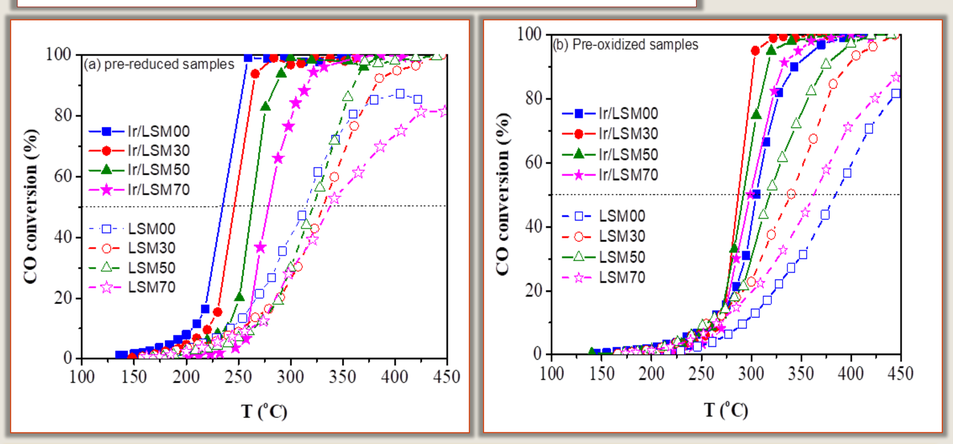

Figure 2. CO conversion versus temperature over LSM supports and counterpart Ir/LSM catalysts with pre-reduced (a) and pre-oxidized (b) samples. Feed conditions: 1.0% CO, 5.0% O_2, He balance at 1 bar; F_T =160 mL/min, catalyst mass m =20 mg, wGHSV=480,000 mL/g.h. Open sympols and dashed lines depict LSM perovskite supports, filled symbols and solid lines depict Ir/LSM catalysts (squares: Ir-LSM00; circles: Ir-LSM30, triangles: Ir-LSM50, stars: LSM70).

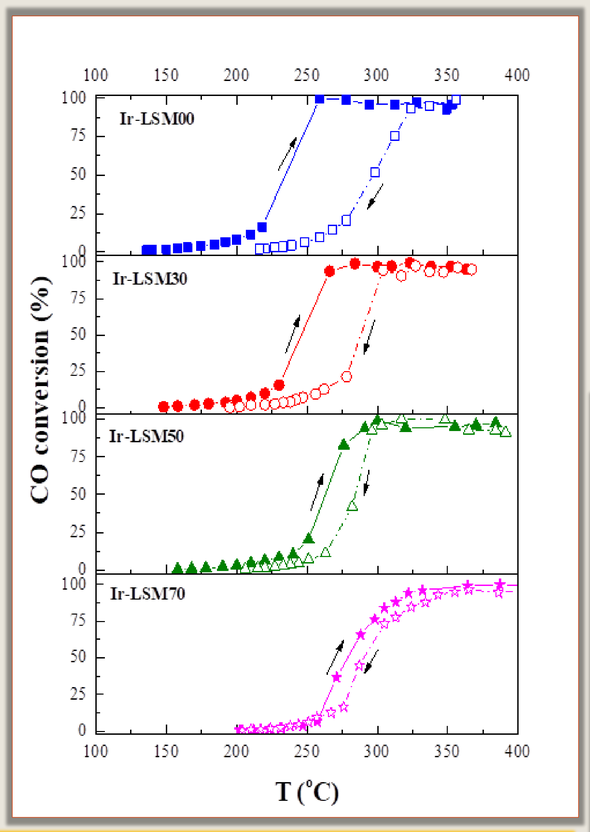

Figure 3. CO conversion *light-off* and *light-out* profiles over pre-reduced Ir-LSM catalysts. Narrows show the direction of data acquisition. Experimental conditions: 1.0% CO, 5.0% O_2 balanced with He at 1 bar; F_T =160 mL/min, catalyst mass m =20 mg, wGHSV=480 000 mL/g·h.

Table 2. The temperature for 50% CO conversion (T_{50}) on LSM perovskite supports and counterpart Ir/LSM catalysts for pre-reduced and pre-oxidized samples.

Sample code	T_{50} (°C) pre-reduced	T_{50} (°C) pre-oxidized	ΔT_{50} (°C) pre-reduced – pre-oxidized	ΔT_{50} (°C) Ir/LSM – LSM (pre-reduced)	ΔT_{50} (°C) Ir/LSM – LSM (pre-oxidized)
LSM00	314	385	-71		
LSM30	331	340	-9		
LSM50	322	318	+4		
LSM70	337	362	-25		
Ir/LSM00	235	305	-70	-79	-80
Ir/LSM30	246	286	-40	-85	-54
Ir/LSM50	262	292	-30	-60	-26
Ir/LSM70	279	299	-20	-58	-63

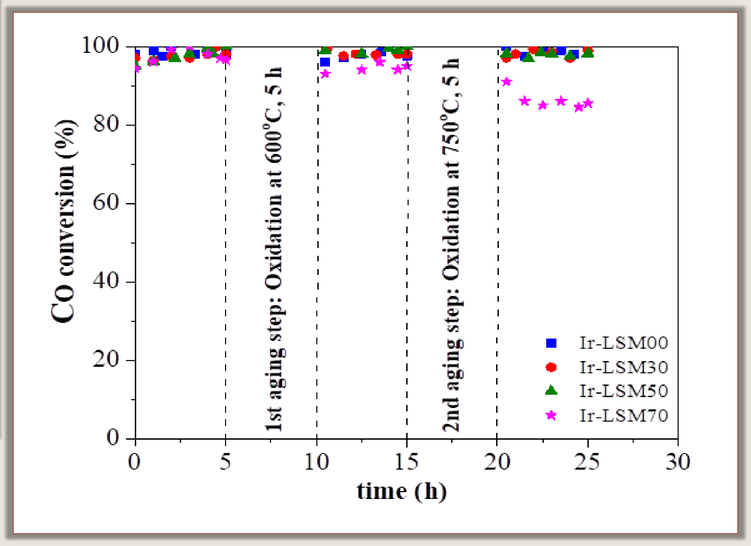

Figure 4. CO conversion efficiency of Ir/LSM catalysts tested after each of two in-situ sequential thermal aging steps at oxidative conditions (20%O_2/He flux of 50 mL/min). 1st step: 5 h at 600°C; 2nd step: 5 additional hours at 750°C

4. Conclusions

- ✓ LSM supports & Ir/LSM materials are active to CO oxidation in the temperature range of ca. 200-450°C.
- ✓Ir/LSM significantly more active than LSM alone and in particular in their pre-reduced state, indicating that Ir^0 phase outweighs IrO_2 in CO oxidation reaction.
- ✓Increase of substitution of La by Sr in LSM support, causes a decrease in CO conversion efficiency of the catalysts.
- ✓Clockwise hysteresis phenomena were observed, with their temperature altitude to be depressed as the La substitution by Sr increases.
- ✓The high OSC of the LSM supports endowed Ir nanoparticles with exceptional anti-sinter properties.
- ✓Ir-LSM catalysts remained stable even after exposure to extreme thermal aging conditions under oxidizing conditions.

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ΓΓΕΤ ΓΕΝΙΚΗ ΓΡΑΜΜΑΤΕΙΑ ΕΡΕΥΝΑΣ ΚΑΙ ΤΕΧΝΟΛΟΓΙΑΣ

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ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ

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