

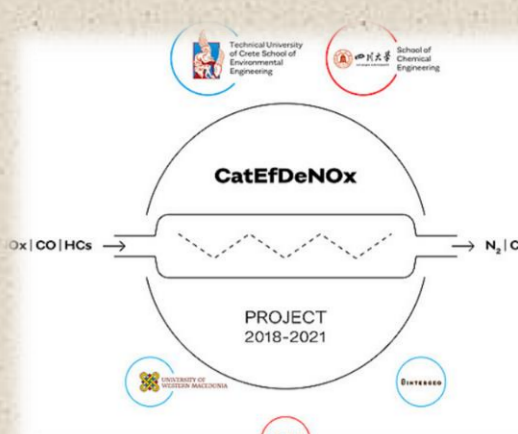


# CO OXIDATION ON SUPPORTED IRIIDIUM NANOPARTICLES UNDER EXCESS O<sub>2</sub> CONDITIONS: STUDY OF RATE HYSTERESIS PHENOMENA

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## 1. Introduction

Here we report on CO oxidation reaction under O<sub>2</sub> excess conditions over Ir nanoparticles dispersed on Al<sub>2</sub>O<sub>3</sub>-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (ACZ, x=0, 0.25, 0.5 and 0.75) mixed oxide supports, which have high oxygen ion lability/mobility and surface oxygen vacancies. Multiple steady states of reaction rate *versus* temperature, the so-called rate *hysteresis* phenomena, have been observed during an increasing-decreasing cycle of temperature at the interval of 100-400°C. Particular emphasis was invoked on understanding the origin of these phenomena and their correlation with the nature of the supporting materials in relation to the oxygen storage capacity characteristics of the latter and the consequent metal-support interactions. The effect of catalyst preparation method on CO oxidation activity and on hysteresis phenomena has been also involved in the present study.

For this purpose, ACZ supports were prepared via two synthesis methods, co-precipitation and hydrothermal, while in both cases Ir was dispersed on the supports by the wet impregnation method. Several protocols of kinetic experiments were designed to shed light on the aforementioned phenomena:

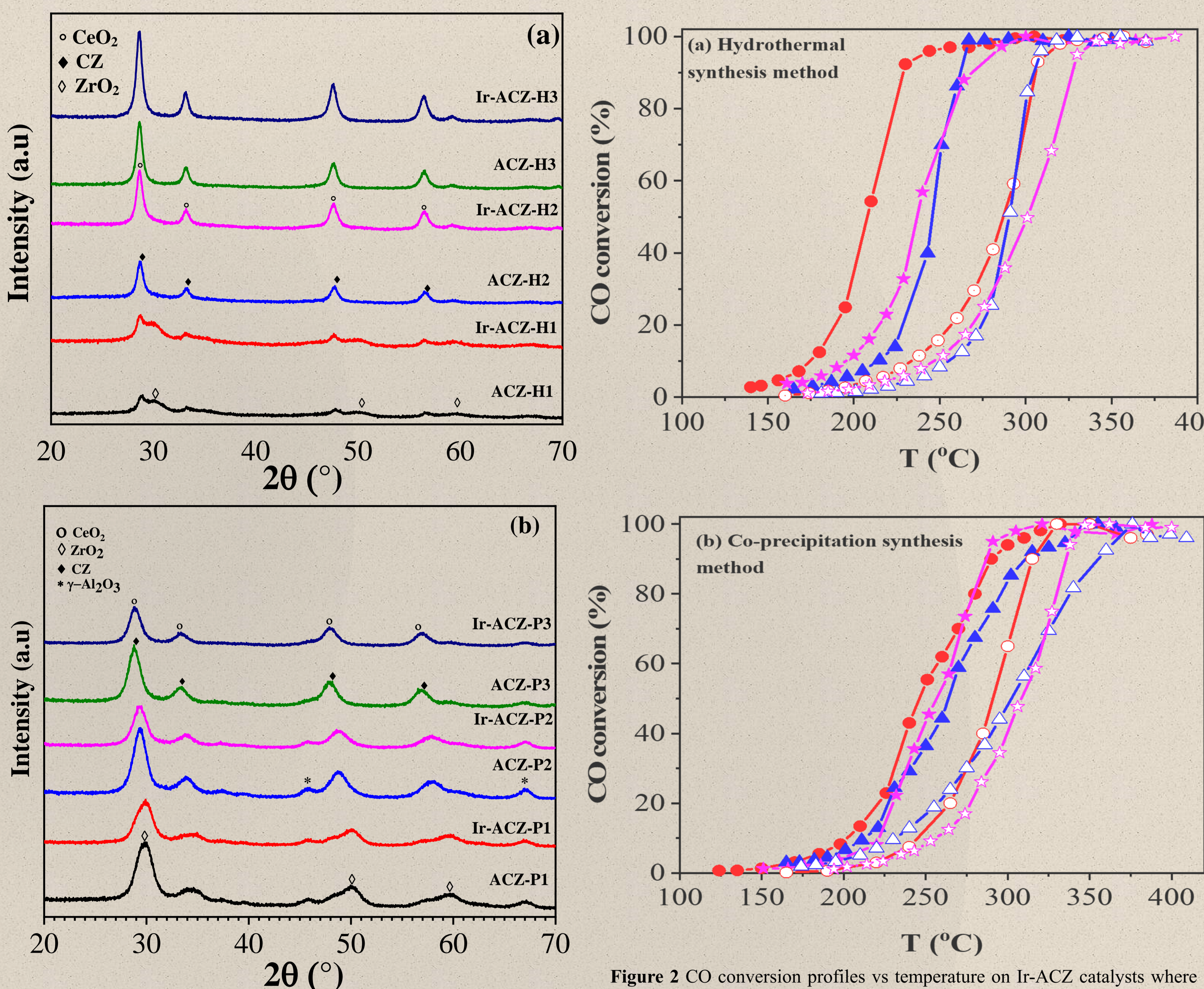
- A series of cyclic experiments, i.e. ignition (light-off) followed by extinction (light-out) at the temperature range of 50-400°C and constant reactor feed conditions ;
- kinetic experiments on pre-reduced and pre-oxidized catalysts; and finally
- kinetic experiments on gradually aged catalysts at high temperature oxidative conditions according to a specific aging protocol.

The textural and structural properties of the supports and the Ir-ACZ catalysts were evaluated by various techniques, in order to gain a better understanding of the relevant structure-activity relationships and hysteresis phenomena implicated.

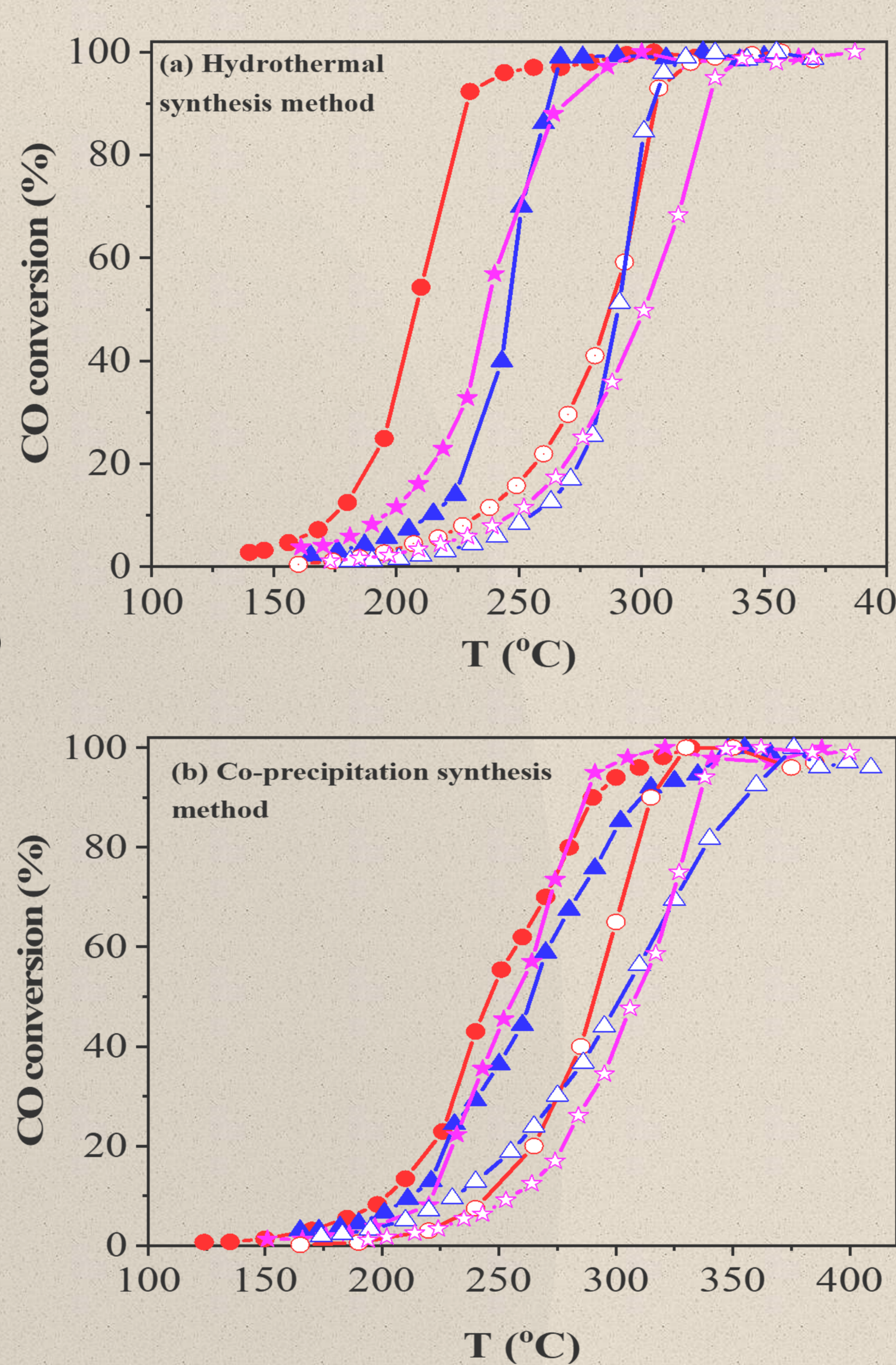
## 2. Experimental

- Synthesis of ACZ supports via (a) hydrothermal method & (b) co-precipitation
- Deposition of Ir on ACZ supports by wet impregnation
- Characterization of ACZ supports and Ir-ACZ catalysts by (a) N<sub>2</sub> physical adsorption-desorption isotherms (BET-BJH), (b) X-ray powder diffraction, (c) Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR), (d) Isothermal hydrogen chemisorption (H<sub>2</sub>-Chem)
- Catalytic activity and thermal stability measurements
  - Feed Gas mixture: 1 % v/v CO, 5 %v/v O<sub>2</sub>/He, F<sub>T</sub>=160 mL/min (wGHSV=320000 mL/g<sub>cat</sub>h)
  - Pre-reduced Ir-catalysts (25% H<sub>2</sub>/He, 350°C, 0.5 h)
  - Pre-oxidized Ir-catalysts (20% O<sub>2</sub>/He, 400° C, 1 h)
  - Thermal stability experiments at 320°C after consecutive oxidation steps at 600°C and 700°C

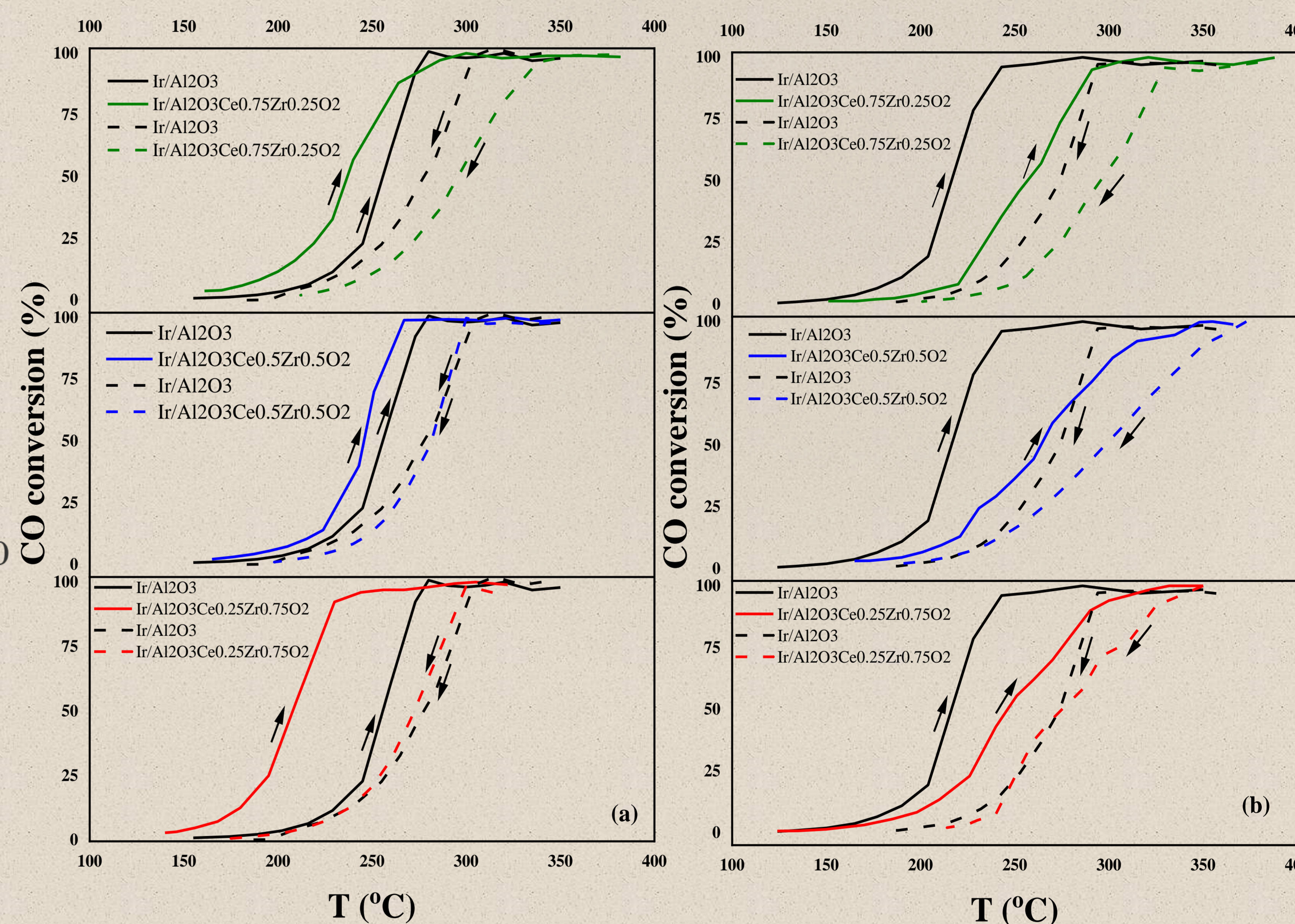
## 3. Results



**Figure 1** XRD patterns of ACZ supports and Ir-ACZ catalysts prepared via hydrothermal method (a) and co-precipitation (b).



**Figure 2** CO conversion profiles vs temperature on Ir-ACZ catalysts where ACZ supports were prepared by hydrothermal method (a) and co-precipitation method (b). Experimental Conditions: Gas Mixture 1% v/v C, 5% v/v O<sub>2</sub> balanced with He, F<sub>T</sub>= 160 cm<sup>3</sup>/min, wGHSV=320 000 mL/g<sub>cat</sub>h (cycles: Ir-Al<sub>2</sub>O<sub>3</sub>Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>, triangles: Ir-Al<sub>2</sub>O<sub>3</sub>Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, stars: Ir-Al<sub>2</sub>O<sub>3</sub>Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>, filled symbols: pre-reduced Ir-ACZ catalysts, open symbols: pre-oxidized Ir-ACZ catalysts)



**Figure 3** CO conversion *light-off* and *light-out* profiles over pre-reduced Ir-ACZ catalysts, where ACZ supports were prepared via hydrothermal method (a) and co-precipitation (b). Arrows show the direction of data acquisition. Experimental conditions: 1.0% CO, 5.0% O<sub>2</sub> balanced with He, at 1 bar; F<sub>T</sub> =160 mL/min, catalyst mass m =30 mg, wGHSV=320 000 mL/g.h. Solid lines: *light-off* profiles, Dashed lines: *light-out* profiles.

**Table 1.** Textural and morphological characteristics of supports and catalysts studied.

Sample	Ce/Zr	S <sub>BET</sub> (m <sup>2</sup> /gr)	Total pore volume (cm <sup>3</sup> /gr)		Average pore diameter (nm)		Ir particle size (nm) <sup>c</sup>	Crystal size of CZ (nm)		
			Support	Catalyst	Support	Catalyst		Support	Catalyst	
Ir-ACZ-H1	0.25/0.75	154	216	0.694	0.639	18.1	11.8	1.4	9.1	9.6
Ir-ACZ-H2	0.5/0.5	172	184	0.532	0.476	12.4	10.4	1.3	11.3	11.4
Ir-ACZ-H3	0.72/0.25	149	157	0.791	0.674	21.3	17.2	1.1	12.6	12.5
Ir-ACZ-P1	0.25/0.75	113	134	0.257	0.289	9.14	8.59	1.0	9.7	10.1
Ir-ACZ-P2	0.5/0.5	102	100	0.235	0.256	9.25	10.2	0.8	8.9	8.5
Ir-ACZ-P3	0.72/0.25	115	125	0.231	0.232	8.01	7.41	1.0	9.7	8.7

## 4. Conclusions

- Pre-reduced Ir-ACZ catalysts-from both groups- were more active than pre-oxidized ones indicating that the metallic Ir<sup>0</sup> is more active than IrO<sub>2</sub> in CO oxidation.
- Moreover, hydrothermally synthesized catalysts are more active compared to their counterpart catalysts made via co-precipitation.
- A clear clockwise hysteresis (limit cycle) performance was recorded for all Ir-ACZ catalysts, from low to higher temperatures (light off) and then returns back (light out) with Ir-ACZ-P catalysts presenting smaller hysteresis width.
- The hysteresis phenomena were related with the Ir active phase and specifically with the Iridium oxidation state of the catalysts.

## Acknowledgements

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