Impact of the support on the activity and stability of Ir catalysts under the Dry Reforming of Methane conditions

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1.INTRODUCTION

Simultaneous use of the two most important greenhouse gases, CO_2 and CH_4, providing an effective method for sustainable carbon recycling through a more environmentally friendly approach to natural gas exploitation, as well as direct utilization of biogas [1].

DRM: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$, $\Delta H^o_{298} = 247$ kJ/mol

Within the temperature range of 650-800°C, intermediate reactions occur which affect both the H_2/CO ratio of the produced synthesis gas and the cumulative deposition of carbon, with the latter being one of the major problems in many catalytic systems. The two main reactions that lead to carbon deposition are :

Boudouard reaction

$2CO \rightleftarrows CO_2 + C \quad \Delta H^o = -172$ kJ /mol

Methane cracking

$CH_4 \rightleftarrows 2H_2 + C \quad \Delta H^o = +75$ kJ/ mol

In this study, the effect of support on the DRM performance (activity at 500-750ºC) of Ir nanoparticles, carbon deposition phenomena, and their stability under reaction (at 750ºC) and/or after oxidative thermal aging conditions is investigated. Supports studied include γ-Al_2O_3, Alumina-Ceria-Zirconia (ACZ) and Ceria-Zirconia (CZ).

2.EXPERIMENTAL

2.1 Synthesis and characterization

✓ The supports of mixed oxides , ACZ (80%wt γ-Al_2O_3 -20%wt $Ce_{0.5}Zr_{0.5}O_{2-\delta}$) and CZ ($Ce_{0.5}Zr_{0.5}O_{2-\delta}$) were prepared by the co-precipitation method, while the alumina oxide γ-Al_2O_3 was sourced from commerce .

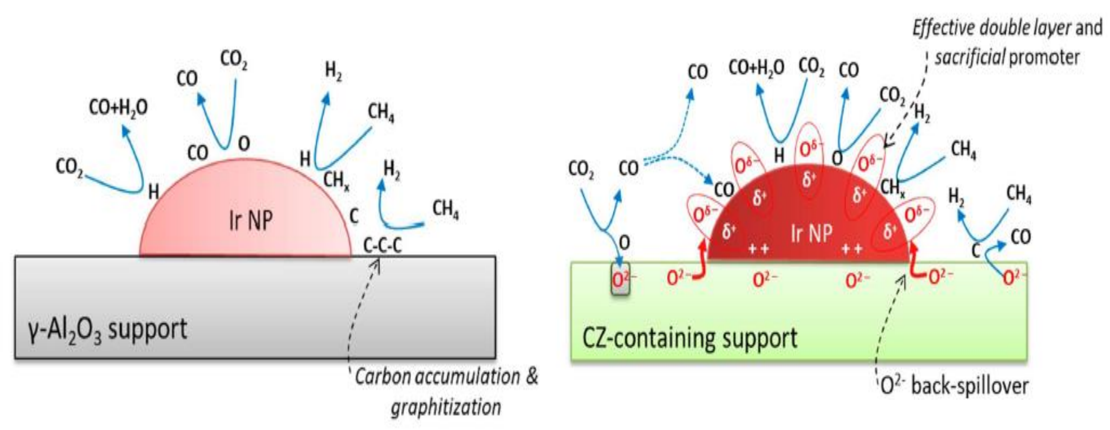
✓ The supported Ir catalysts were prepared by the wet impregnation method, with a targeted metal loading of ~1wt%. After wet impregnation, the catalysts were reduced under continuous flow of 50% H_2/He (50ml/min) at 400ºC for 2h, followed by a flow of 1% H_2/He (50ml/min) at 850ºC for 1h (referred to as "fresh").The exact determination of Ir loading on the catalysts was performed by ICP-OES (1wt% Ir/Al_2O_3, 0.4wt% Ir/ACZ, and 0.6wt% Ir/CZ).

✓The structural and morphological characteristics of the catalysts, as well as their other physicochemical properties, were determined using BET, XRD, HRTEM, H_2-TPR, H_2-chemisorption, ICP-OES and TPO-carbon deposition studies

2.2 Catalytic experiments (activity and stability experiments/ oxidative thermal aging)

✓Catalytic experiments were carried out in an isothermal fixed-bed reactor (quartz i.d.=3mm) with a catalyst loading of 50 mg. The reactor feed composition consisted of 50% CH_4 and 50% CO_2 simulating biomass gasification. The total feed flow rate (F_t) was 100 mL/min (WGHSV = 120,000 mL/gcat·h). The performance of the catalysts was studied in the temperature range of 500-750ºC and their stability at 750ºC for 12h.

✓After evaluating the fresh catalysts in the DRM reaction, we proceeded with their oxidative aging, which was performed in two successive steps: (i) 2h oxidation under 20% O_2 flow in He (50ml/min) at 650ºC (aged@650), and (ii) an additional 2h oxidation under 20% O_2 flow in He (50ml/min) at 750ºC (aged@750). After each step, the catalysts were re-evaluated in the DRM under constant temperature conditions (750ºC) and a feed of CH_4:CO_2=50%:50% with a flow of 100 mL/min (GHSV = 120,000 mL/g·h) and pressure of 1 bar.



Scheme 1. Graphical representation of the DRM reaction pathways over Ir nanoparticles dispersed on Al_2O_3 and CZ-containing supports. The promotional effects induced by CZ-containing supports with high OSC values originate from the presence of the surface oxygen vacancies, labile O^{2-} species and back-spillover phenomena.

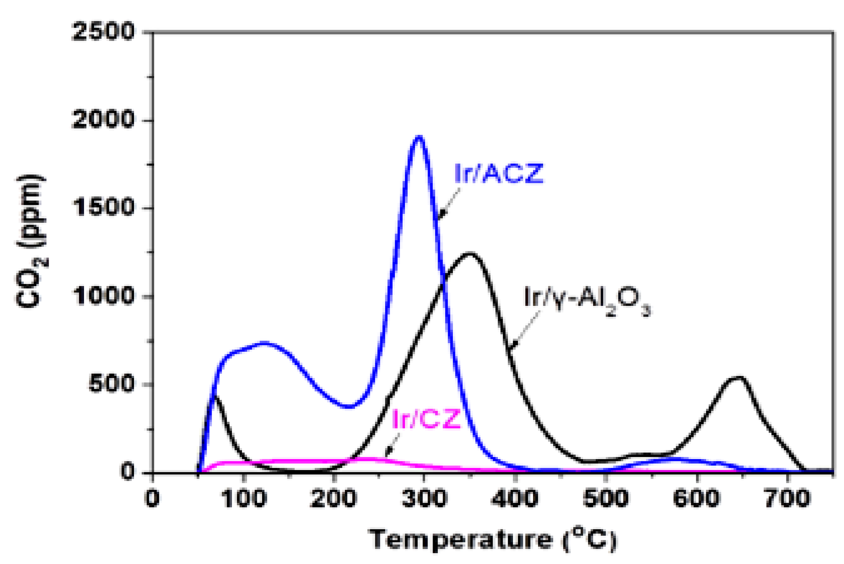


Figure 4. Temperature programmed oxidation profiles of fresh catalysts Ir/γ-Al_2O_3, Ir/ACZ, and Ir/CZ after 3 hours of operation under DRM reaction conditions (CH_4:CO_2=50%, F=100 mL/min, T=750°C)

3.RESULTS & DISCUSSION

3.1 Activity and stability experiments

Table 1: Textural, morphological and reducibility characteristics of the -Al_2O_3, ACZ and CZ supports and the corresponding as-prepared (fresh) Ir/-Al_2O_3, Ir/ACZ and Ir/CZ catalysts.(BET, H_2TPR, H_2 chemisorption results)

Supports/ Catalysts	S_{BET} (cm²/g)	Total Pore Volume (cm³/g)	OSC (μmol O_2/g)	Dispersion D_{Ir} (H/Ir)	Mean Ir particle size (nm)
γ-Al_2O_3	178	0.6	0	-	-
Ir/γ-Al_2O_3	167	0.57	38	0.7	1.2
ACZ	149	0.29	110	-	-
Ir/ACZ	73	0.22	176	0.41	1.8
CZ	22	0.05	557	-	-
Ir/CZ	17	0.04	601	0.61	1.3

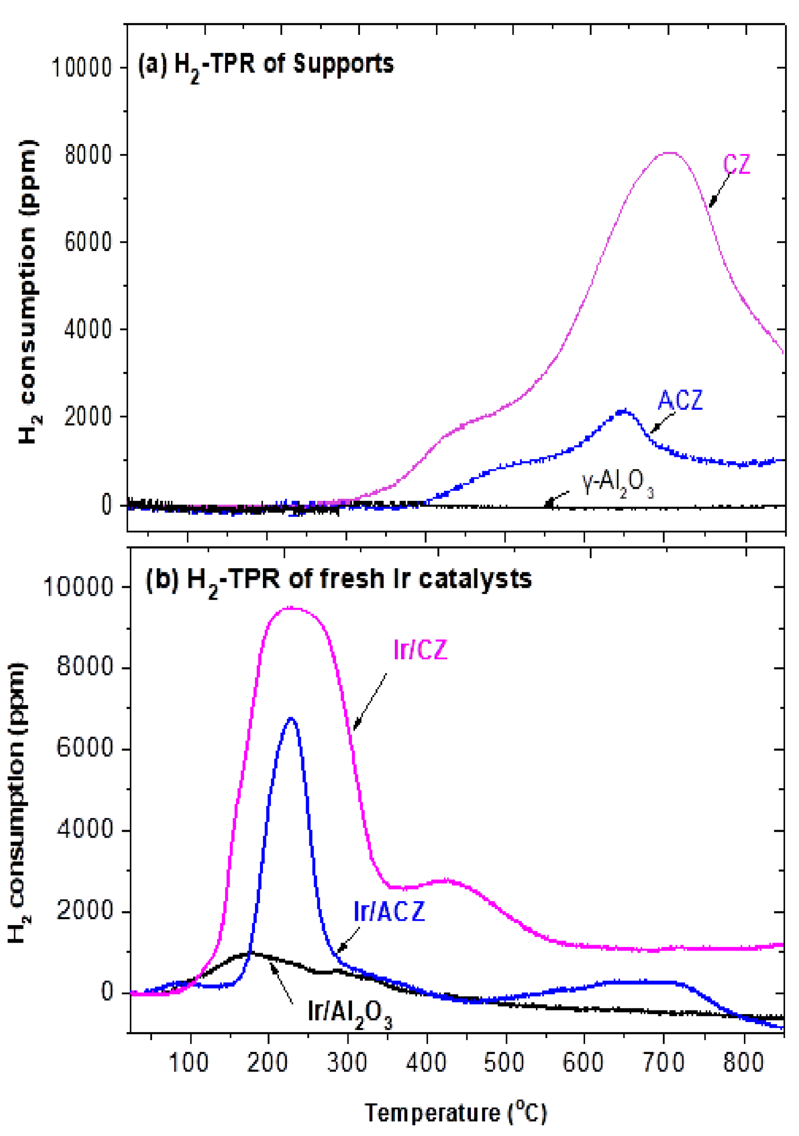


Figure 1. H_2-TPR profiles of the Al_2O_3, ACZ and CZ supports (a), and the Ir/-Al_2O_3, Ir/ACZ and Ir/CZ catalysts (b)

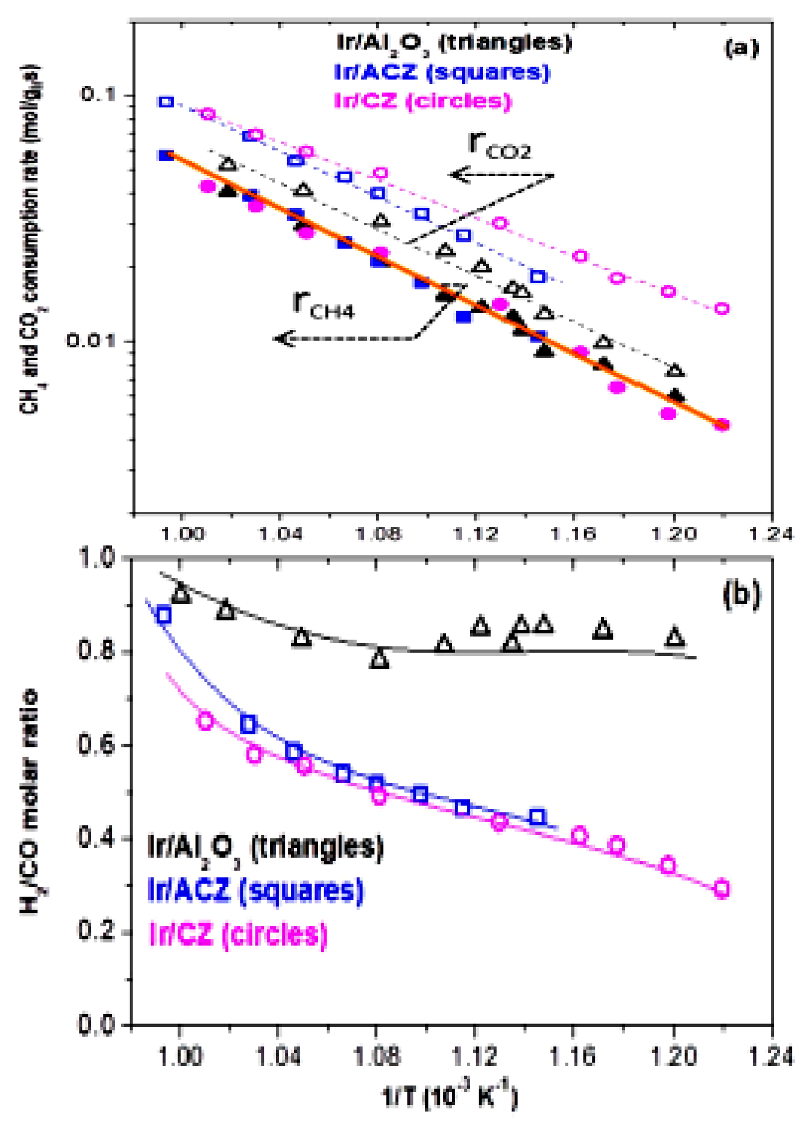


Figure 3. Arrhenius plots showing the temperature dependence of (a) the CH_4 (closed symbols) and CO_2 (open symbols) consumption rates, and (b) the corresponding H_2/CO molar ratios, obtained for fresh Ir/Al_2O_3, Ir/ACZ and Ir/CZ catalysts. Experimental conditions: ([CH_4] = [CO_2] = 50 % , 1 bar, w_{cat} = 50 mg, WGHSV = 120,000–200,000 mL/gcat·h.

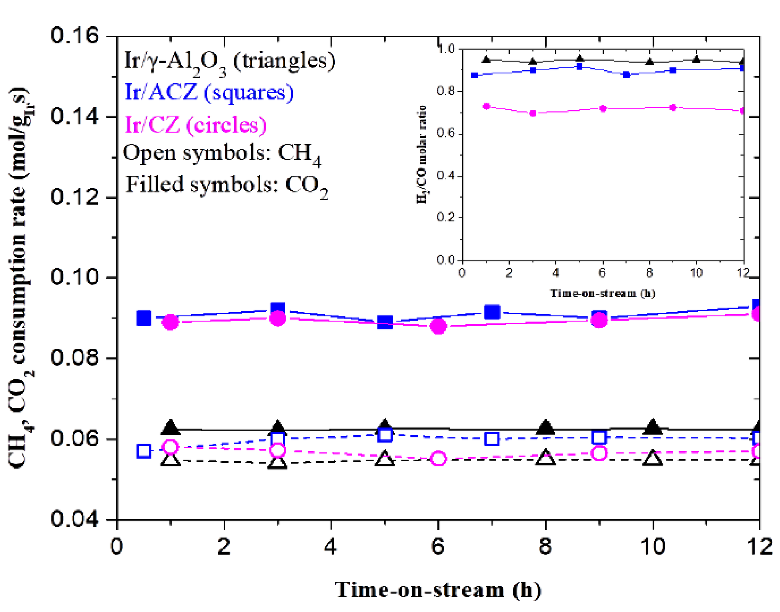


Figure2. CH_4 and CO_2 consumption rates and H_2/CO molar ratios (inset) obtained with the fresh Ir/Al_2O_3, Ir/ACZ and Ir/CZ catalysts as a function of time-on-stream . Experimental conditions :T = 750ºC, [CH_4]in = [CO_2]in = 50% ,1 bar, WGHSV = 120,000 mL/gcat·h ,w_{cat} = 50 mg.

Table 2. Support-induced effects on apparent activation energies during DRM over Ir/Al_2O_3, Ir/ACZ and Ir/CZ catalysts.

Catalysts	Support OSC (μmol O_2/g)	Activation Energy (Ea) (KJ/mol)
Ir/γ-Al_2O_3	0	91.3
Ir/ACZ	110	88.5
Ir/CZ	557	73.5

3.2 Oxidative thermal aging

Step 1
2h oxidation under 20% O_2 flow in He (50ml/min) at 650ºC(aged@650ºC)

Step 2
Additional 2h oxidation under 20% O_2 flow in He (50ml/min) at 750ºC (aged@750ºC)

Table 3. Textural and morphological characteristics of the "aged@750" catalysts.

Catalysts	S_{BET} cm²/g	OSC support μmolO_2/g	Mean Ir particle size (nm) of fresh catalysts	Mean Ir particle size (nm) of aged catalysts
Ir/γ-Al_2O_3	140	0	1.2	13.6
Ir/ACZ	64	110	1.8	2.1
Ir/CZ	16	557	1.3	1.6

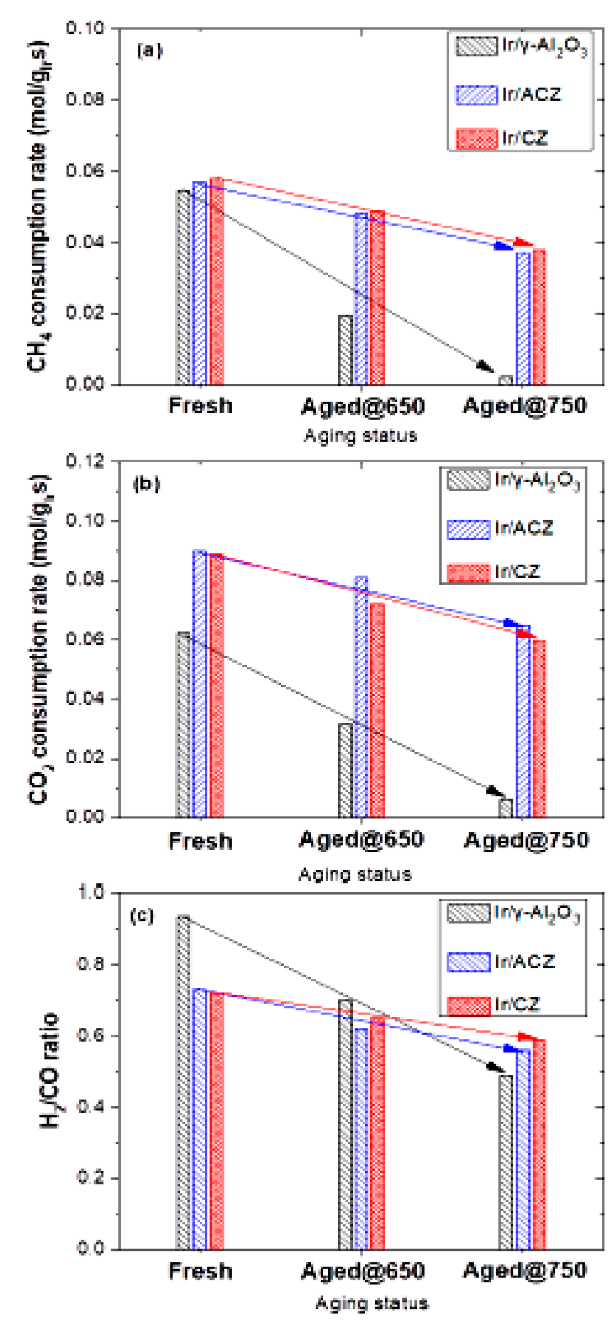


Figure 5. The effects of consecutive oxidative thermal aging on the DRM performance, CH_4 consumption rate (a), CO_2 (open symbols) consumption rates, and (b) the H_2/CO molar ratio (c), of Ir/γ-Al_2O_3,Ir/ACZ and Ir/CZ catalysts. Aging protocols: (i) Aged@650 (2h in situ oxidation with 50 mL/min flow of 20% O_2/He at 650°C) (ii) Aged@750 (consecutive 2h additional in situ oxidation with 50 mL/min flow of 20% O_2/He at 750°C). Experimental conditions:750°C , [CH_4] = [CO_2] = 50% ,1 bar, mcat =50mg, WGHSV = 120,000 mL/gcat·h. DRM performance values given are the mean values of 5–6 measurements taken in a period of ~ 6 h of stable time - on - stream operation.

4.CONCLUSIONS

✓The use of ACZ and CZ supports with sufficient OSC and surface oxygen vacancies significantly enhances the CO_2 consumption rate while not affecting the CH_4 consumption rate. This implies the occurrence of a bifunctional reaction mechanism.

✓The catalysts exhibited excellent time-on-stream stability due to the low propensity of Ir to form and accumulate carbon, as well as the resistance of metallic Ir phase to agglomeration.

✓The Ir/ACZ and mainly Ir/CZ catalysts show a lower tendency for carbon accumulation, verifying the important role of labile O_δ species of the support on the gasification rate of surface carbon species.

✓ Ir nanoparticles deposited on supports with a high OSC value display remarkable stability (resistance to agglomeration) under conditions of intense oxidative thermal aging.

5.REFERENCES

[1] E. Nikolaraki, […], I.V. Yentekakis, Nanomaterials, 11 (2021) 2880.

Acknowledgements

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