Support-induced effects on the Ir nanoparticles activity, selectivity and stability performance under the CO_2 reforming of methane reaction

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1. Introduction

- Dry (CO_2) reforming of methane (DRM), toward syngas (Eq. 1) concerns (i) the simultaneous abatement of two key greenhouse gases (CO_2 and CH_4), (ii) provides the efficient direct biogas utilization and (iii) gives opportunities for recycling of CO_2 emissions by natural gas.

$$CH_4 + CO_2 \leftrightharpoons 2CO + 2H_2, \quad \Delta H^o_{298} = 247 \text{ kJ mol}^{-1} \quad (1)$$

- Syngas ($CO+H_2$) is a critical feedstock for the production of H_2, ammonia and Fischer-Tropsch derived liquid energy carriers.

- DRM rank among the top issues of applied catalysis in the light of environmental protection, renewable energy production and circular economy.

Objectives

- ✓ Study the low temperature DRM performance on Ir-based catalysts at differential reactor operation conditions (i.e., kinetic regime-intrinsic activity).
- ✓ Evaluation of the role of Ir metal-support interactions, upon the use of supports with a variety of oxygen storage capacity (OSC) values on (a) the activity, (b) the selectivity, (c) the resistance to carbon deposition as well as (d) on the stability under high-temperature oxidative aging of Ir nanoparticles.

2. Experimental

A. Catalysts preparation

Supporting materials: γ-Al_2O_3 (commercial), ACZ (80 wt.% Al_2O_3-20 wt.% $Ce_{0.5}Zr_{0.5}O_{2-\delta}$) & CZ ($Ce_{0.5}Zr_{0.5}O_{2-\delta}$) made by co-precipitation

Supported Ir catalysts: preparation of low iridium loading (0.4-1.0% wt) catalysts by wet impregnation

Aged catalysts: Two consecutive aging protocols: 2h in situ oxidation with 50 cm^3/min flow of 20% O_2/He at 650^{o}C (protocol: "Aged@650") followed by 2 h additional oxidation at 750^{o}C (protocol: "Aged@750")

B. Materials characterization

N_2 adsorption-desorption (BET-BJH method); isothermal hydrogen chemisorption (H_2-Chem.); inductively coupled plasma optical emission spectroscopy (ICP-OES); high resolution transmission electron microscopy (HRTEM); powder X-ray diffraction (PXRD), hydrogen temperature programmed reduction (H_2-TPR); temperature programmed oxidation (TPO).

C. (a) Catalytic activity experiments

Experimental Conditions: 50%v/vCH_4+50%v/v CO_2, w_{cat}=50mg, F_T=100-200 cm^3/min T=500-750^{o}C

(b) Time-on-stream (TOS) stability experiments

Experimental Conditions: 50 % v/v CH_4 + 50%v/v CO_2, total pressure 1bar, F_T=100 cm^3/min, (wGHSV=120,000 $cm^3/g_{cat}h$), T=750^{o}C, 12 h.

3. Results

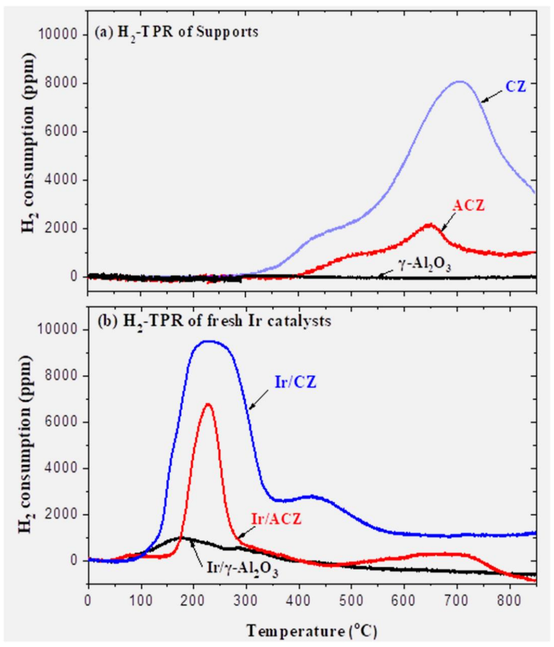

Figure 1. H_2-TPR profiles of the γ-Al_2O_3, ACZ and CZ supports (a), and the counterpart Ir/γ-Al_2O_3, Ir/ACZ and Ir/CZ catalysts (b)

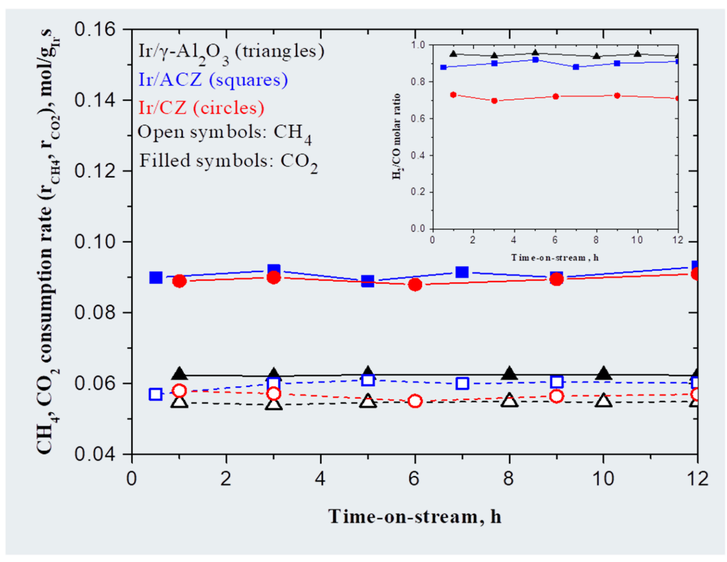

Figure 2 CH_4 and CO_2 consumption rates, and corresponding H_2/CO molar ratio yielded for fresh Ir/γ-Al_2O_3, Ir/ACZ and Ir/CZ catalysts vs time-on-stream at T =750 ^{o}C and equimolar feed composition ($[CH_4]^{in}$ = $[CO_2]^{in}$ = 50% at a total pressure of 1 bar). Other conditions: $F_{t,in}$ = 100 cm^3/min; w_{cat} = 50 mg. Open symbols & dashed lines: CH_4 consumption rates, filled symbols & solid lines: CO_2 consumption rates for Ir/γ-Al_2O_3 (triangles), Ir/ACZ (squares) and Ir/CZ (circles) catalysts

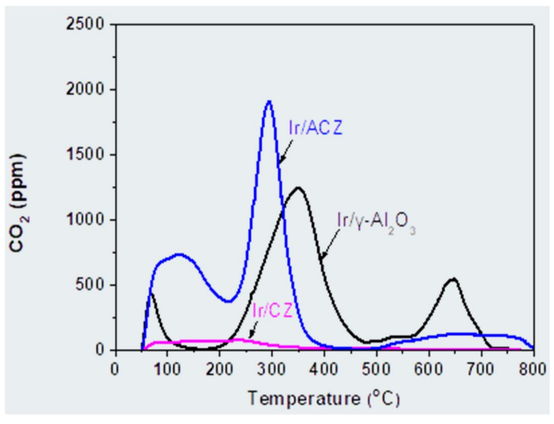

Figure 3. Temperature programmed oxidation profiles (CO_2 production versus temperature) of fresh Ir/γ-Al_2O_3, Ir/ACZ and Ir/CZ catalysts after exposure to DRM reaction conditions (i.e., $[CO_2]$=$[CH_4]$=50% at 1 bar, m_{cat} = 100 mg, WGHSV = 60,000 cm^3/g_{cat}·h, T=750 ^{o}C). Temperature ramp of TPO was 10^{o}C/min from room temperature to 800^{o}C under a stream of 6.1% O_2 in He.

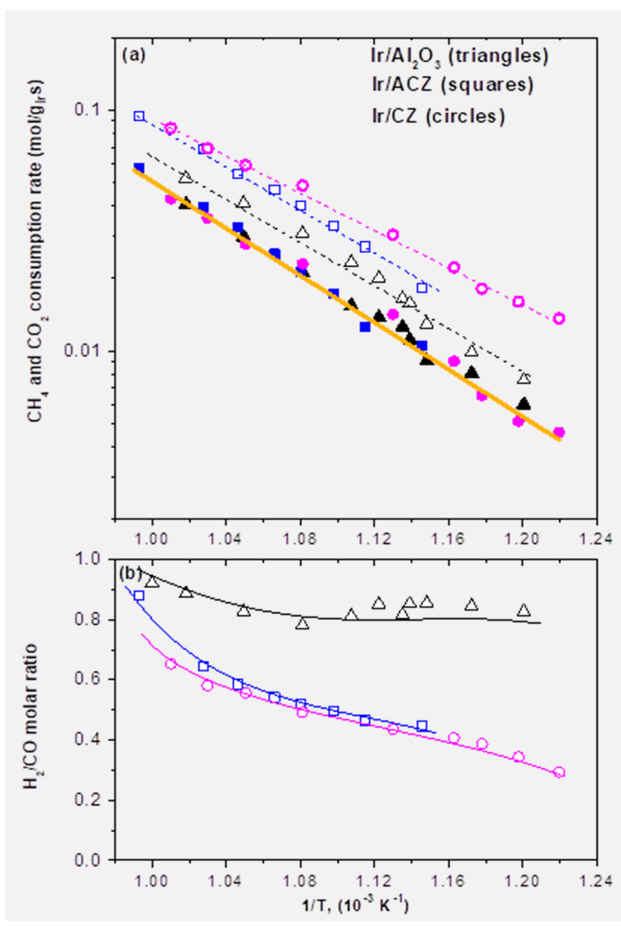

Figure 4. Catalysts intrinsic activity in Arrhenius plots. (a): Temperature dependence of CH_4 (closed symbols) and CO_2 (open symbols) consumption rates, and (b): corresponding H_2/CO molar ratios, for fresh Ir/Al_2O_3, Ir/ACZ & Ir/CZ catalysts. Experimental conditions: $[CH_4]$ = $[CO_2]$ = 50 % at a total pressure of 1 bar, catalyst mass w_{cat} = 50 mg, WGHSV= 120 000 cm^3/g_{cat}·h

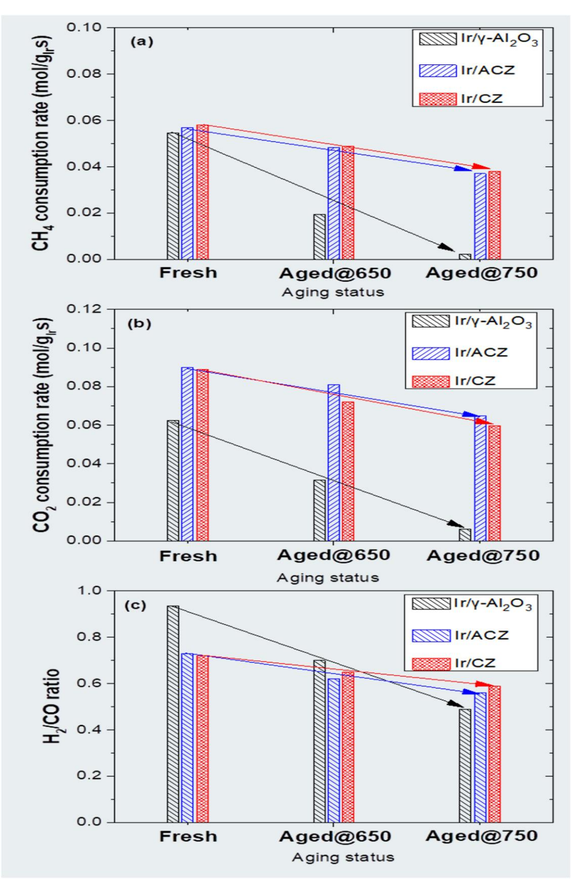

Figure 5. The effect of consecutive oxidative thermal aging on DRM performance of Ir/γ-Al_2O_3, Ir/ACZ και Ir/CZ catalysts. Aging protocols: (i) Aged@650 (2 h in situ oxidation with 50 cm^3/min flow of 20% O_2/He at 650^{o}C); (ii) Aged@750 (consecutive 2 h additional in situ oxidation with 50 cm^3/min flow of 20% O_2/He at 750^{o}C. DRM performance was evaluated at 750^{o}C, equimolar feed composition $[CH_4]$=$[CO_2]$=50% at a total pressure of 1 bar, m_{cat} = 50 mg, WGHSV= 120 000 cm^3/g_{cat}·h.

4. Conclusions

- ✓ Independently of the support, Ir/γ-Al_2O_3, Ir/ACZ and Ir/CZ catalysts have a very stable time-on-stream DRM performance. However, supports with high oxygen storage capacity (i.e. ACZ and CZ) further promote CO_2 consumption, yielding CO-enriched syngas.
- ✓ For all catalysts carbon deposition was low, although it is decreasing in the order Ir/γ-Al_2O_3>Ir/ACZ>Ir/CZ that is consistent with a bifunctional mechanism involving participation of oxygen vacancies on the surface of the support in CO_2 activation (CO_2 → CO + O) and carbon removal.
- ✓ The lower apparent activation energy for CO_2 consumption rate, observed with CZ-containing catalysts (Ir/ACZ and Ir/CZ) suggests that CZ is a promising support for use in low temperature DRM.

Acknowledgements

This research has been co-financed by the European Union and Greek national funds through the operational program 'Regional Excellence' and the operational program Competitiveness, Entrepreneurship and Innovation, under the call "RESEARCH-CREATE-INNOVATE" (Project code: T2EΔK-00955)

Co-financed by Greece and the European Union