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A comparative study of the effect of the active phase (Rh, Ru, Ir, and Ni) and catalyst support on CO_2 methanation reaction

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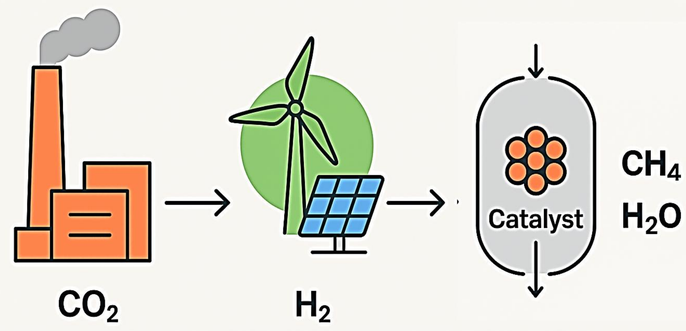
(a) Introduction

The rapid increase in atmospheric CO_2 levels, due to our continued dependence on fossil fuels (coal, oil and natural gas) for energy production, which intensifies the greenhouse effect and accelerates climate change, imposes the urgent need to review our energy strategies. The global community is now moving in a coordinated manner towards the so-called "energy transition" and the reduction of CO_2 emissions. The capture and reuse of emitted CO_2, in the sense of recycling it by converting it into fuels (e.g. methane, methanol), is currently receiving significant research and technological interest.

In this work, we study the catalytic performance on CO_2 methanation reaction of the noble metals ruthenium (Ru), rhodium (Rh) and iridium (Ir) compared to that of nickel (Ni). These active metals are supported on various metal oxide supports, namely γ-Al_2O_3 (AL), Al_2O_3-CeO_2-ZrO_2 (ACZ), and CeO_2-ZrO_2 (CZ), which exhibit different values of labile lattice oxygen (oxygen storage capacity, OSC), a factor critical for enhancing redox reactions.

✓ Our goal is to comparatively evaluate the effectiveness of the various active metal phases in the reaction, but also how the properties of the various supports used affect the catalytic behavior through metal-support interactions.

SABATIER REACTION



$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

$\Delta H = -165$ kJ/mol

(b) Experimental

-Catalysts synthesis

Support materials: commercially available γ-Al_2O_3 (Engelhard), while laboratory made by co-precipitation CZ & ACZ (Table 1).

Noble metal (Ru, Rh, Ir) & Ni based catalysts were prepared by wet impregnation (Table 1).

- Catalysts Characterization

Structural and physicochemical characterization of supports and catalysts was conducted using BET, XRD, H_2 chemisorption (H_2-Chem) and temperature-programmed reduction by H_2 (H_2-TPR) techniques.

- Comparative catalytic performance evaluation experiments

i. A tubular (I.D. = 3 mm), quartz, fixed-bed type reactor, m_{cat}=50 mg, temperature range of 200–600 °C. Feed conditions: 20% H_2/5% CO_2/75% Ar at 1 bar F_t = 50 mL/min (i.e. Weight basis Gas Hourly Space Velocity = 60,000 mL/g·h

ii. The "light-off" behavior of the catalysts was expressed in terms of % CO_2 conversion (X_{CO2}), % yield of CH_4 and CO (Y_{CH4} and Y_{CO}) and % selectivity of CH_4 and CO (S_{CH4} and S_{CO})

(c) Results

Table 1. Chemical composition, textural characteristics and oxygen storage capacities of the supports and corresponding supported metal catalysts.

Samples	OSC (μmol O_2/g)	S_{BET} (m^2/g)
Supports		
γ-Al_2O_3	0	178
ACZ (80wt%Al_2O_3-20wt%$Ce_{0.5}Zr_{0.5}O_{2-\delta}$)	110	149
CZ ($Ce_{0.5}Zr_{0.5}O_{2-\delta}$)	557	22
Ru-based catalysts		
0.7wt% Ru/γ-Al_2O_3	91	162
0.7wt% Ru/ACZ	188	148
0.8wt% Ru/CZ	654	22
Rh-based catalysts		
1.0wt% Rh/γ-Al_2O_3	69	160
0.8wt% Rh/ACZ	146	136
0.8wt% Rh/CZ	589	17
Ir-based catalysts		
1wt% Ir/γ-Al_2O_3	38	167
0.4wt% Ir/ACZ	176	73
0.6wt% Ir/CZ	601	17
Ni-based catalysts		
10wt% Ni/γ-Al_2O_3	840	150
10wt% Ni/ACZ	1008	85
10wt% Ni/CZ	1417	7

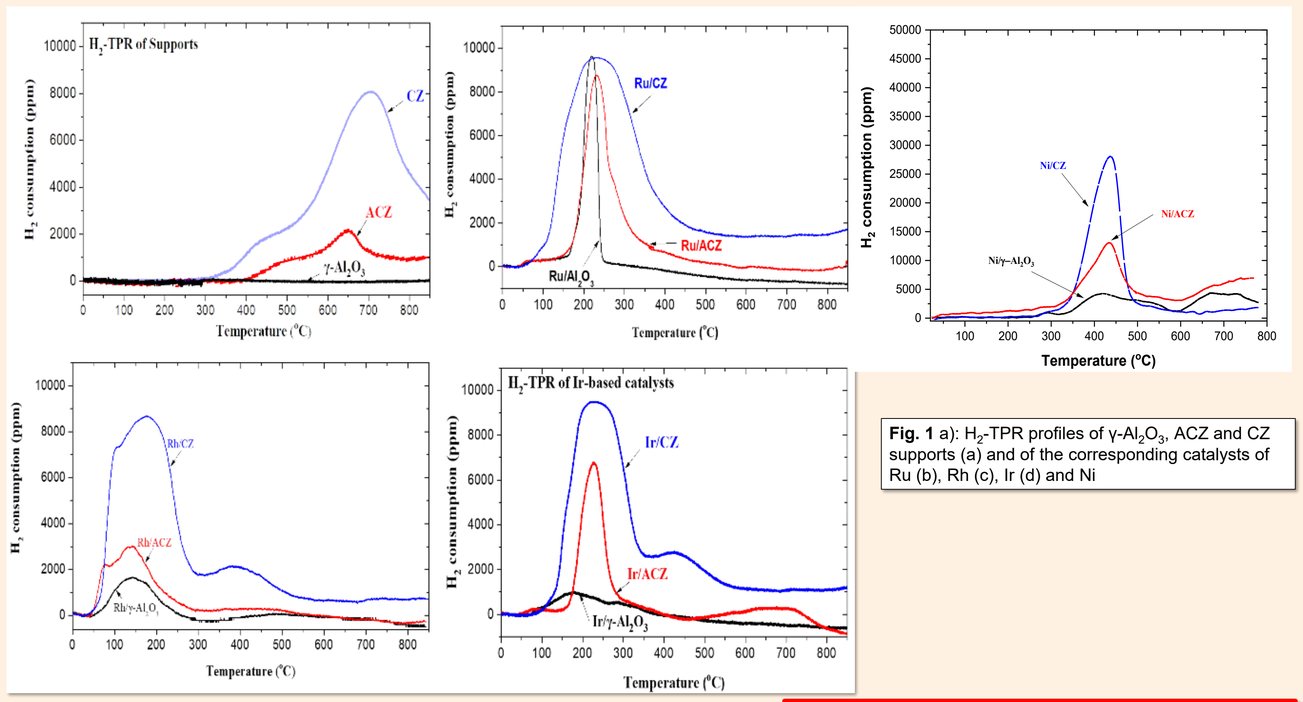


Fig. 1 a): H_2-TPR profiles of γ-Al_2O_3, ACZ and CZ supports (a) and of the corresponding catalysts of Ru (b), Rh (c), Ir (d) and Ni

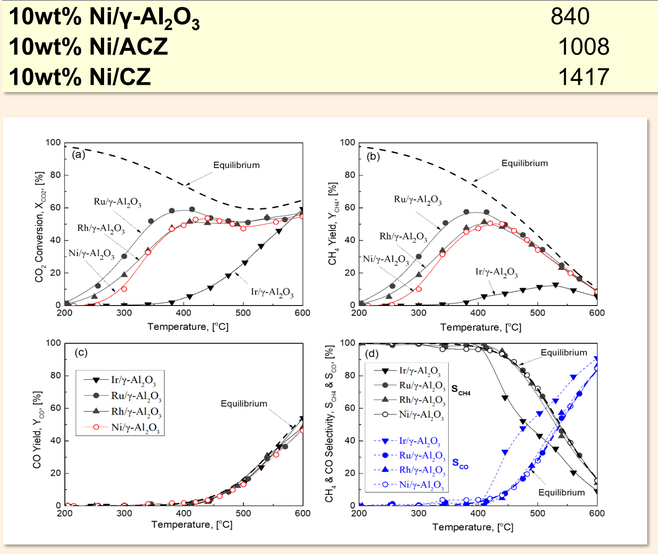


Fig. 2 CO_2 conversion (a), CH_4 and CO yield (b, c) and corresponding CH_4 and CO selectivity (d) of Ru, Rh, Ni and Ir nanoparticles supported on γ-Al_2O_3 support as a function of temperature. Feed conditions: 20% H_2/ 5% CO_2/75% Ar, F_t =50 cm^3/min, w_{cat} = 50 mg WGHSV=60,000 mL/g h.

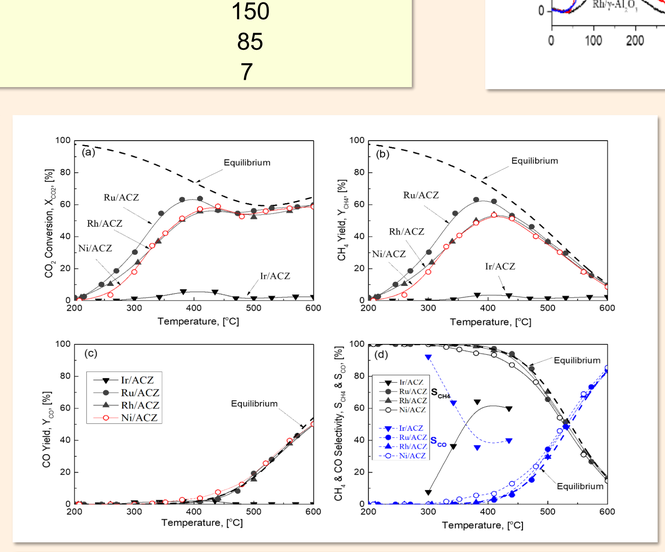


Fig. 3 CO_2 conversion (a), CH_4 and CO yield (b, c) and corresponding CH_4 and CO selectivity (d) of Ru, Rh, Ni and Ir nanoparticles supported on ACZ (support as a function of temperature. Feed conditions: 20% H_2 / 5% CO_2 /75% Ar, F_t = 50 cm^3/min, w_{cat} = 50 mg WGHSV=60,000 mL/g h.

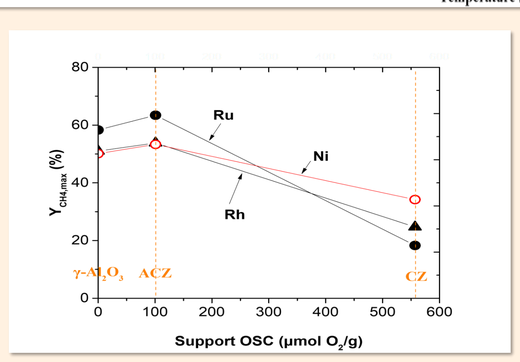


Fig. 4 Effect of catalyst supports on methanation performance: Maximum CH_4 yield of Ru, Rh and Ni catalysts supported on γ-Al_2O_3, ACZ and CZ supports with different Oxygen Storage Capacity values. Feed conditions: 20% H_2/5% CO_2/75% Ar; WGHSV= 60,000 mL/gh, w_{cat}=50 mg.

(d) Conclusions

- ✓ Our findings revealed a clear ranking in the catalytic performance of the active phases, as Ru > Rh > ~ Ni > Ir, regardless of the supports on which they were dispersed.
- ✓ Furthermore, we observed a significant, but not monotonic, effect of the oxygen storage capacity of the support on the CO_2 methanation performance.
- ✓ Interestingly, supports that possess an intermediate oxygen storage capacity, such as ACZ, demonstrated optimal enhancement of the active phase for CO_2 methanation.

These insights emphasize the importance of catalyst support properties in the design of efficient methanation catalysts. By carefully tailoring the OSC of the support, metal-support interactions can be optimized and, consequently, the catalytic performance.

Acknowledgments

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