A comparative study of the CO_2 methanation efficiency of dispersed Rh, Ru, Ir and Ni nanoparticles: Effect of metal nature and supporting material

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1. Abstract

- Energy needs of modern life inevitably keep high and unluckily increasing fossil fuels (coal, oil, and natural gas) utilization in order to address those. This leads to the emission of enormous quantities of CO_2 in the atmosphere. However, CO_2 is a greenhouse gas and its high and continuously increasing concentration in the atmosphere renters it as the determinant cause of global warming and the concomitant climate change.
- Therefore, control of CO_2 emissions is an urgent environmental need. Besides the direct efforts for partial -or even complete- replacement of carbon-based fuels with renewable energy sources, CO_2 capture and storage (CCS) and CO_2 utilization/recycling through its conversion to added-value products and fuels (e.g. methane, methanol) technologies are nowadays among the approaches that receive intense research and technological interest [1-5].
- Here we report on the CO_2 methanation efficiency of Rh, Ru, Ir and Ni nanoparticles dispersed on a variety of mixed oxide supports with the characteristic of different oxygen storage capacity and mobility, namely γ-Al_2O_3 (AL), Al_2O_3-CeO_2-ZrO_2 (ACZ) and CeO_2-ZrO_2 (CZ).
- The effect of the active metal nature as well as of the oxygen storage capacity (OSC) of the supporting material on CO_2 conversion efficiency and methane production selectivity are comparatively addressed.
- It has been found that the activity of the active metals investigated under the titled reaction follows the same order Ir<Ni<Rh<Ru on all supports used, except for CZ on which the order is changed to Ir<Rh<Ni<Ru. However, for each active phase supported on different supports a significant but non monotonic influence of the OSC of the support on CO_2 methanation output characteristics occurred; the support with intermediate OSC value (i.e., ACZ) was found to be optimal for promoting CO_2 methanation, independently of the active phase.

2. Experimental methods

- ✓ Ru, Rh, Ir and Ni nanoparticles (~1 wt% for noble metals, while 10 wt% for Ni) were dispersed, via wet impregnation, on oxide and mixed-oxide supports characterized by very different *oxygen storage capacities and labilities*, i.e., γ-Al_2O_3, ACZ and CZ (Table 1); Their Oxygen Storage Capacity (OSC) values were estimated by using H_2-TPR profiles obtained in the temperature region 25-850^{o}C (Table 1)
- ✓ Nanoparticle sizes were estimated using isothermal H_2-chemisorption experiments, that were corroborated in some cases by HRTEM measurements (Table 1).
- ✓ The CO_2 hydrogenation performance of the catalysts was comparatively studied in fixed bed reactors loaded with 50 mg of catalyst mass and fed with a 50 mL/min of a 20% H_2/5% CO_2/75% Ar gas mixture (i.e., Weight basis Gas Hourly Space Velocity = 60,000 mL/g h; H_2/CO_2=4/1) at the temperature range 200-600^{o}C.
- ✓ The following equations were used for the analysis of kinetic results:
  - X_{CO2} (%) = 100·([CH_4]out + [CO]out) / ([CO_2]out + [CH_4]out + [CO]out)
  - Y_{CH4} (%) = 100· [CH_4]out / ([CO_2]out + [CH_4]out + [CO]out)
  - Y_{CO} (%) = 100·[CO]out / ([CO_2]out + [CH_4]out + [CO]out)
  - S_{CH4} (%) = 100·[CH_4]out / ([CH_4]out + [CO]out)
  - S_{CO} (%) = 100·[CO]out / ([CH_4]out + [CO]out)
  - Fin·[CO_2]in = Fout·([CO_2]out + [CH_4]out + [CO]out): Carbon balance closing

3. Catalysts Characterization Results

Table 1: Textural and OSC characteristics of Supports and Catalysts studied

Supports and Catalysts	OSC (μmol O_2/g)	S_{BET} (m^2/g)
7Supports		
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

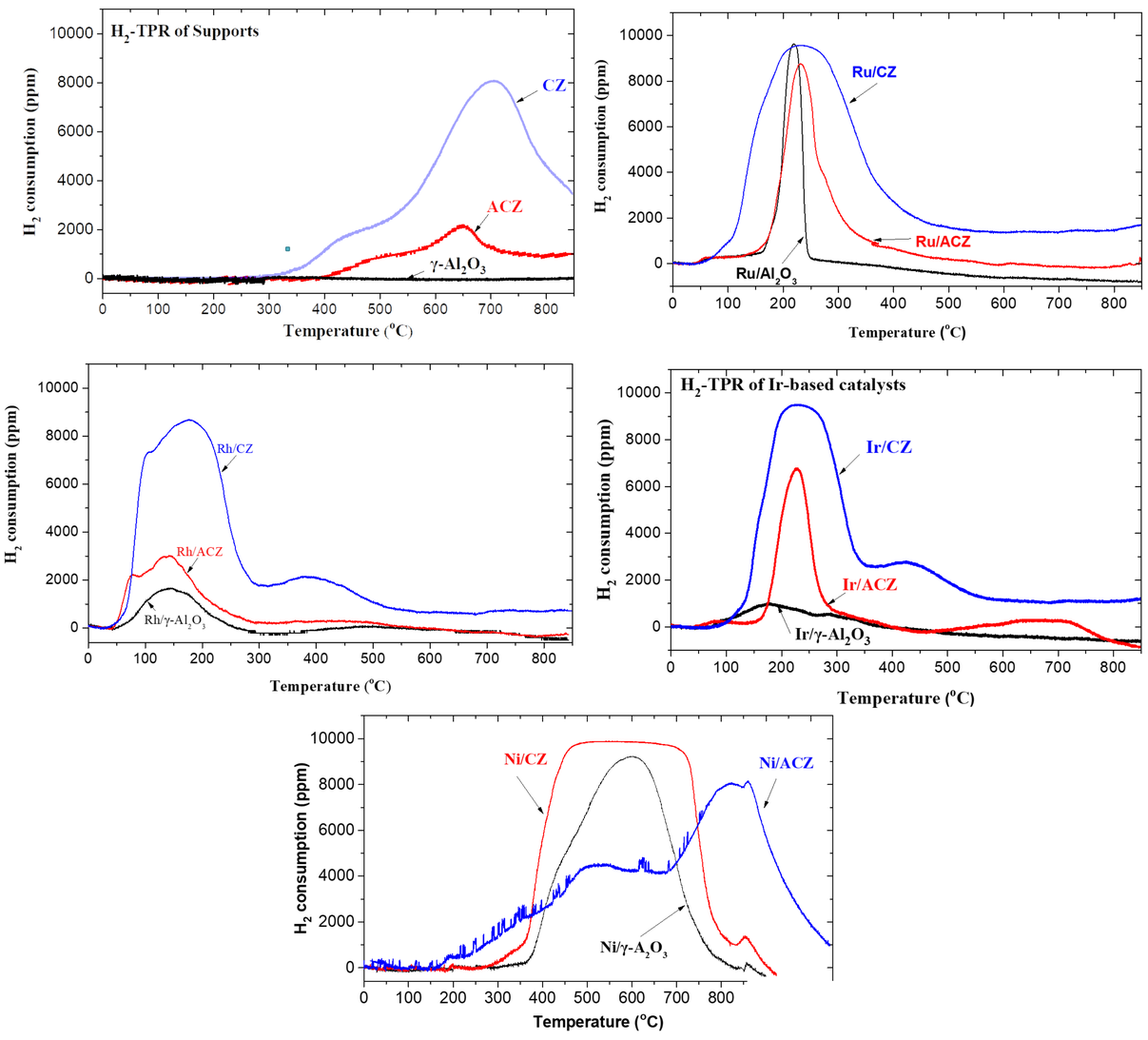

Fig. 1: H_2-TRP profiles of γ-Al_2O_3, ACZ and CZ supports and the counterpart Ru, Rh, Ir and Ni catalysts.

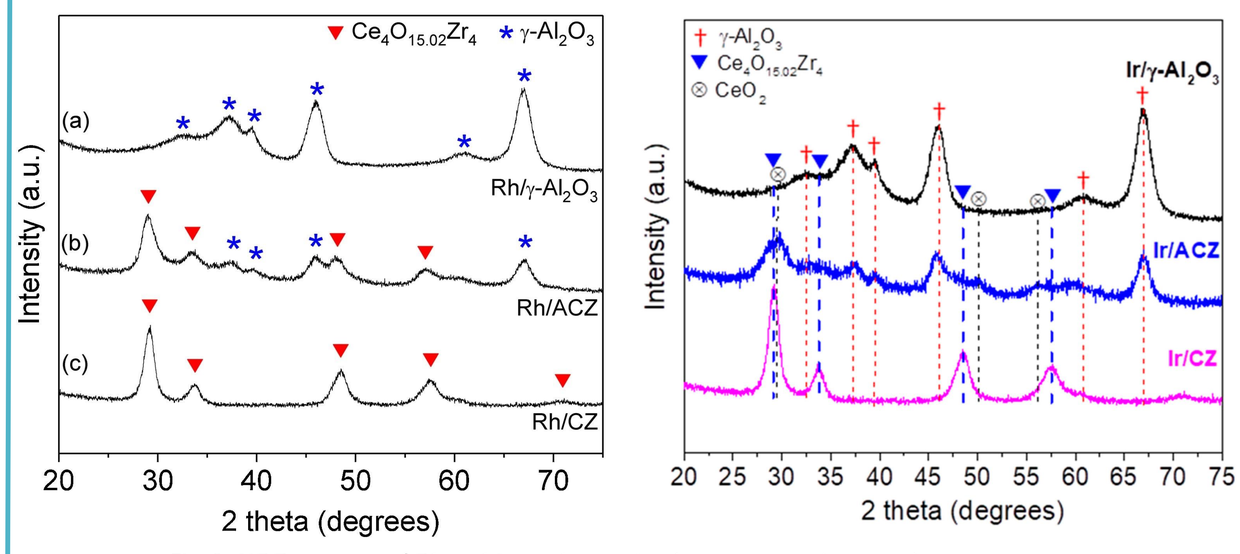

Fig. 2: XRD patterns of Rh and Ir catalyst series (as representative cases).

4. CO_2 hydrogenation performance of the catalysts

4.1. Textural and morphological characteristics of Supports and Catalysts studied

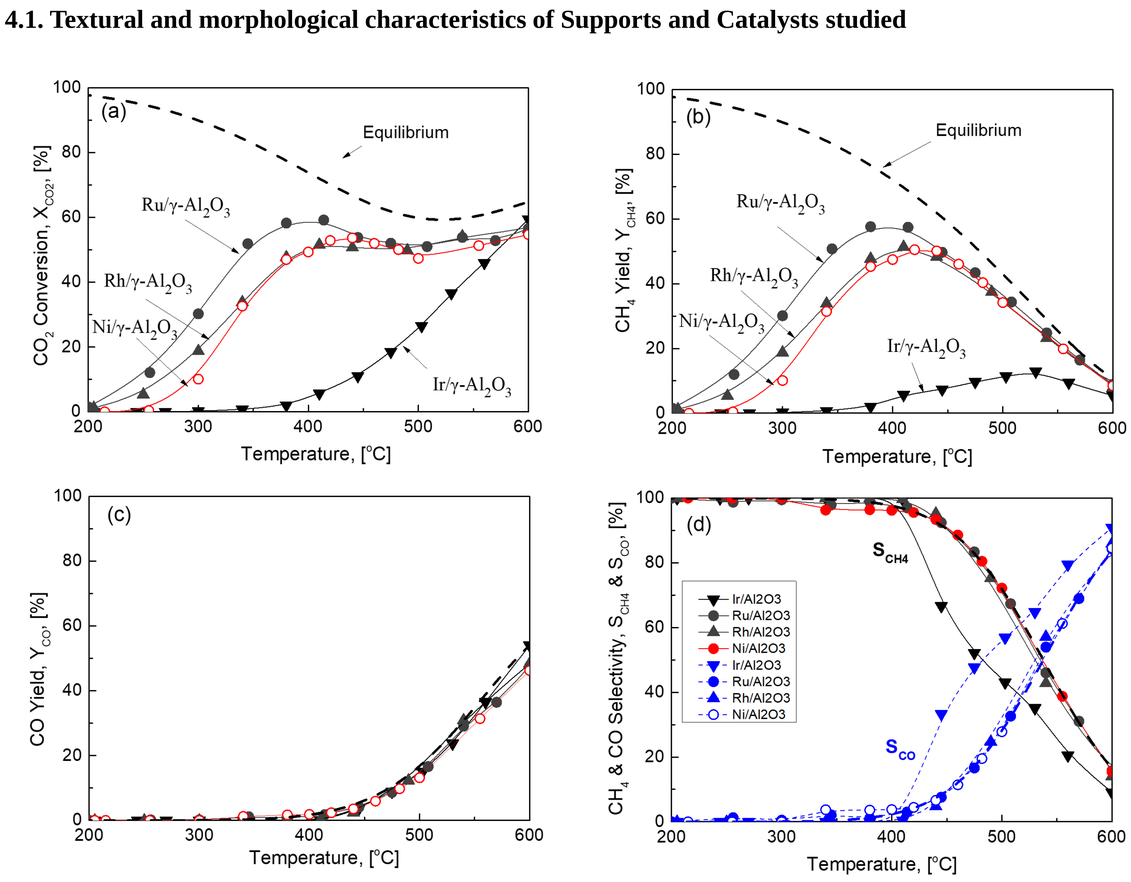

Fig. 3. *Effect of active metal nature on CO_2 methanation performance:* (a) CO_2 conversion, (b) CH_4 Yield, (c) CO Yield, and (d) CH_4 and CO selectivities for all Ru, Ru, Ir and Ni catalysts supported on γ-Al_2O_3, as a function of temperature. Reactor Feed conditions: 20% H_2/5% CO_2/75% Ar; WGHSV= 60,000 mL/g h. Catalyst mass w_{cat}=50 mg.

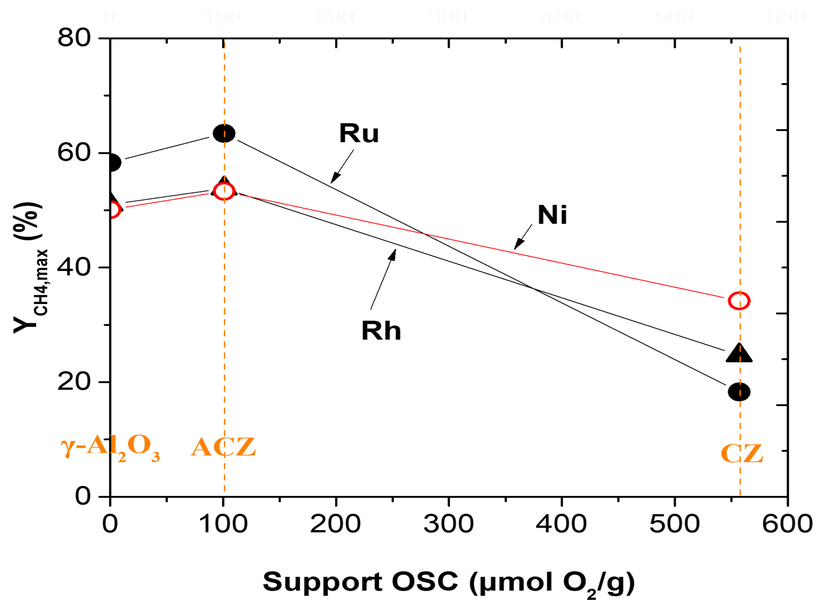

Fig. 4. *Effect of catalyst's supports on methanation performance:* Maximum CH_4 yields of Ru, Rh and Ni catalysts supported on γ-Al_2O_3, ACZ and CZ supports with different Oxygen Storage Capacity values. Feed conditions: 20% H_2/5% CO_2/75% Ar; WGHSV= 60,000 mL/g h. Catalyst mass w_{cat}=50 mg.

5. Conclusions

- ✓ Low noble metal (Ru, Rh and Ir) loading catalysts (~1wt%) and a high loading Ni one (10 wt%) supported on supports with different OSC values were comparatively studied for the CO_2 methanation reaction.
- ✓ The methanation efficiency of the active metals followed the same order, Ir<Ni<Rh<Ru, on all supports used, except for the case of CZ on which the activity order was modified as Ir<Rh<Ni<Ru.
- ✓ It was also found that the OSC value of the support strongly influences methanation activity of all metals investigated: The support with intermediate OSC value (i.e., ACZ) was found to be optimal for promoting CO_2 methanation, independently of the metal nature.

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