Electrochemical Promotion of CO_2 Hydrogenation on Ru films deposited on YSZ (O^{2-} conductor) and β''-Al_2O_3 (Na^+, K^+ conductor)

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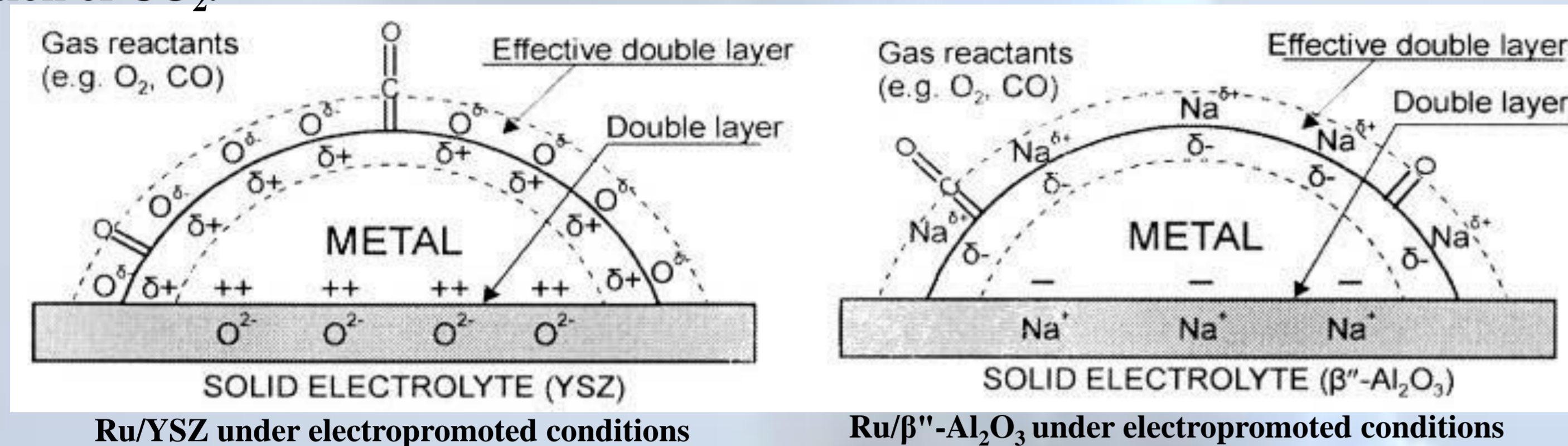
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Introduction

The hydrogenation of CO_2 to hydrocarbons or alcohols has received worldwide attention both as a potential source of renewable fuels and as a potential means to decrease CO_2 emissions [1]. EPOC has been investigated thoroughly for more than 120 catalytic reaction systems [2]. In EPOC studies the conductive catalyst-electrode is in contact with an ionic conductor and the catalyst is electrochemically promoted by applying a current or potential between the catalyst film and a counter or reference electrode, respectively. In this study Ru catalyst electrodes were deposited over YSZ (O^{2-} conductor) and β''-Al_2O_3 (Na^+ or K^+ conductor) solid electrolytes, for the hydrogenation of CO_2.

Ru/YSZ under electropromoted conditions

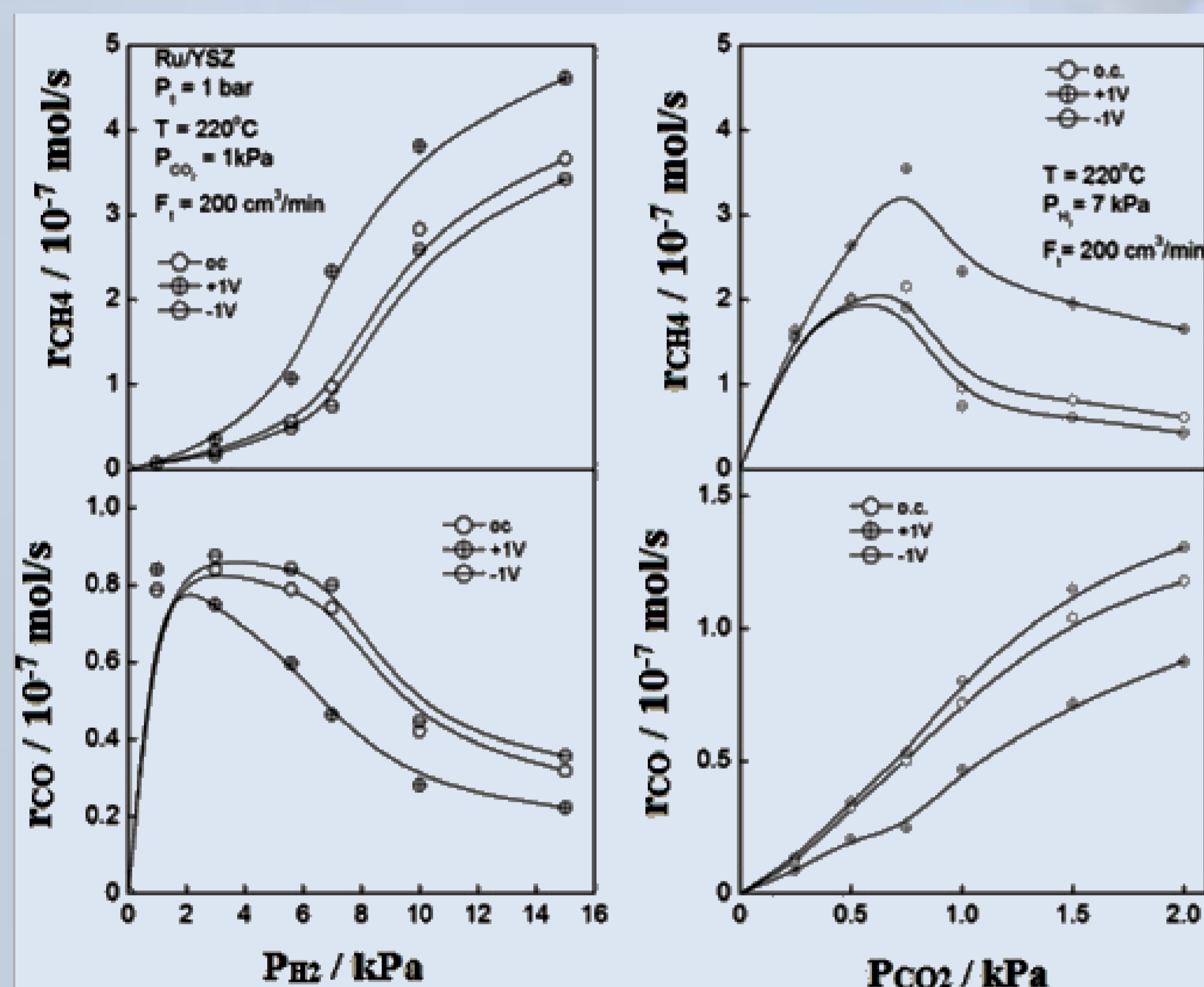**Ru/β''-Al₂O₃ under electropromoted conditions**

Experimental

- Ru working electrode
  $RuCl_3$ solution (500°C for 60 min)

- Au counter and reference electrodes
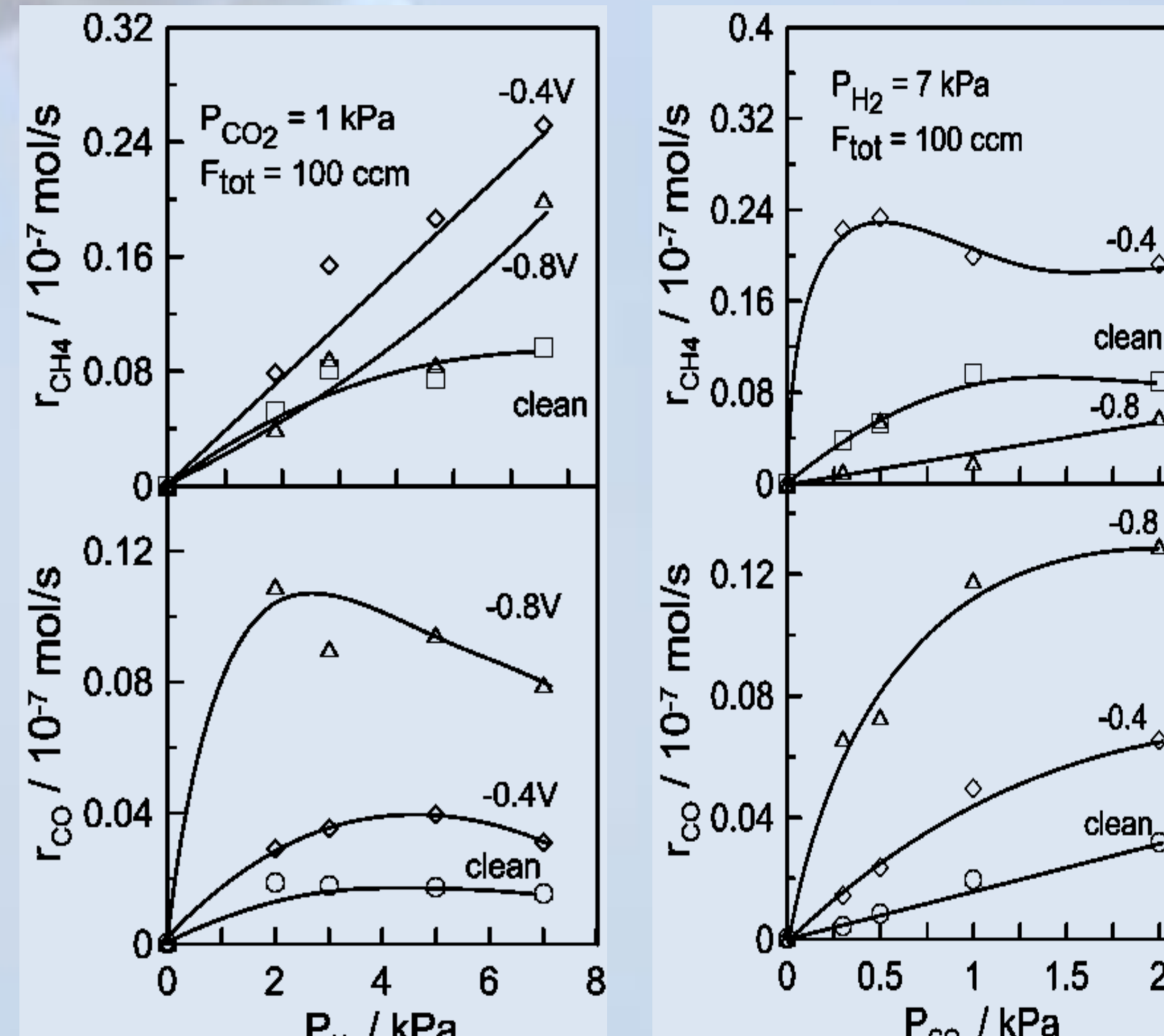 organometallic paste, A118 Metalor
  (650°C 30 min)
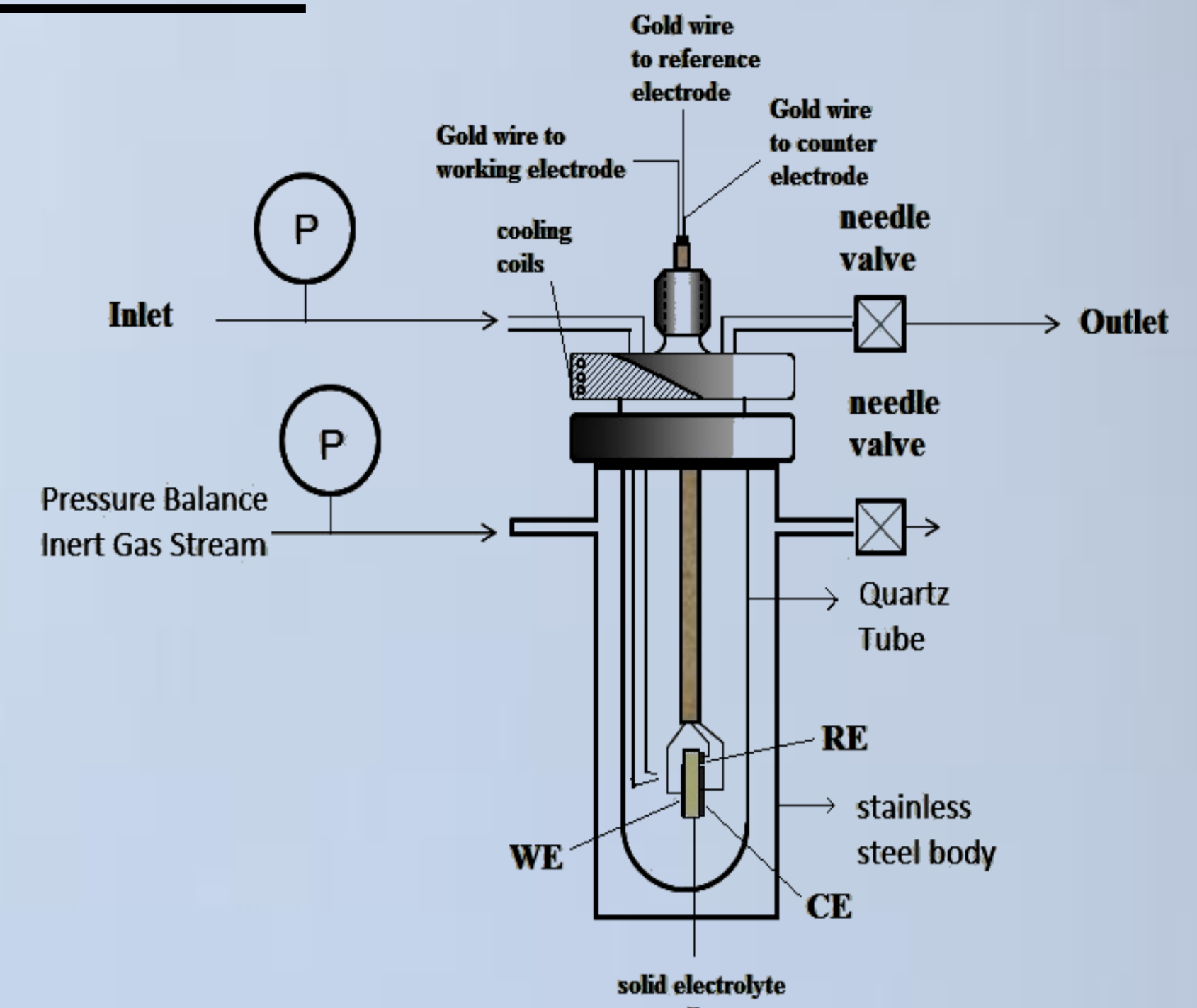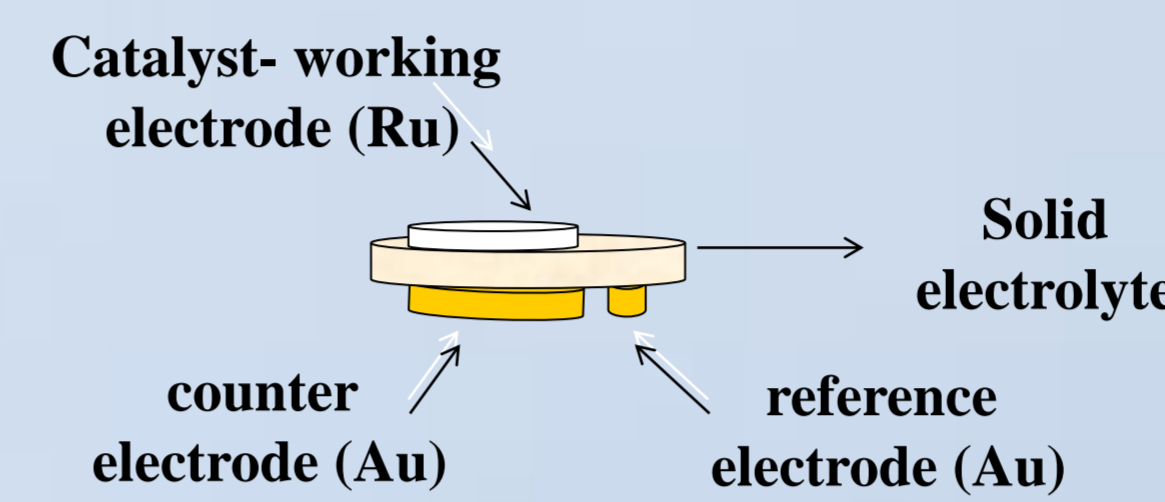
Results and Discussion: Steady state effect of P_{H2} and P_{CO2} on the rate of CO_2 methanation and RWGS
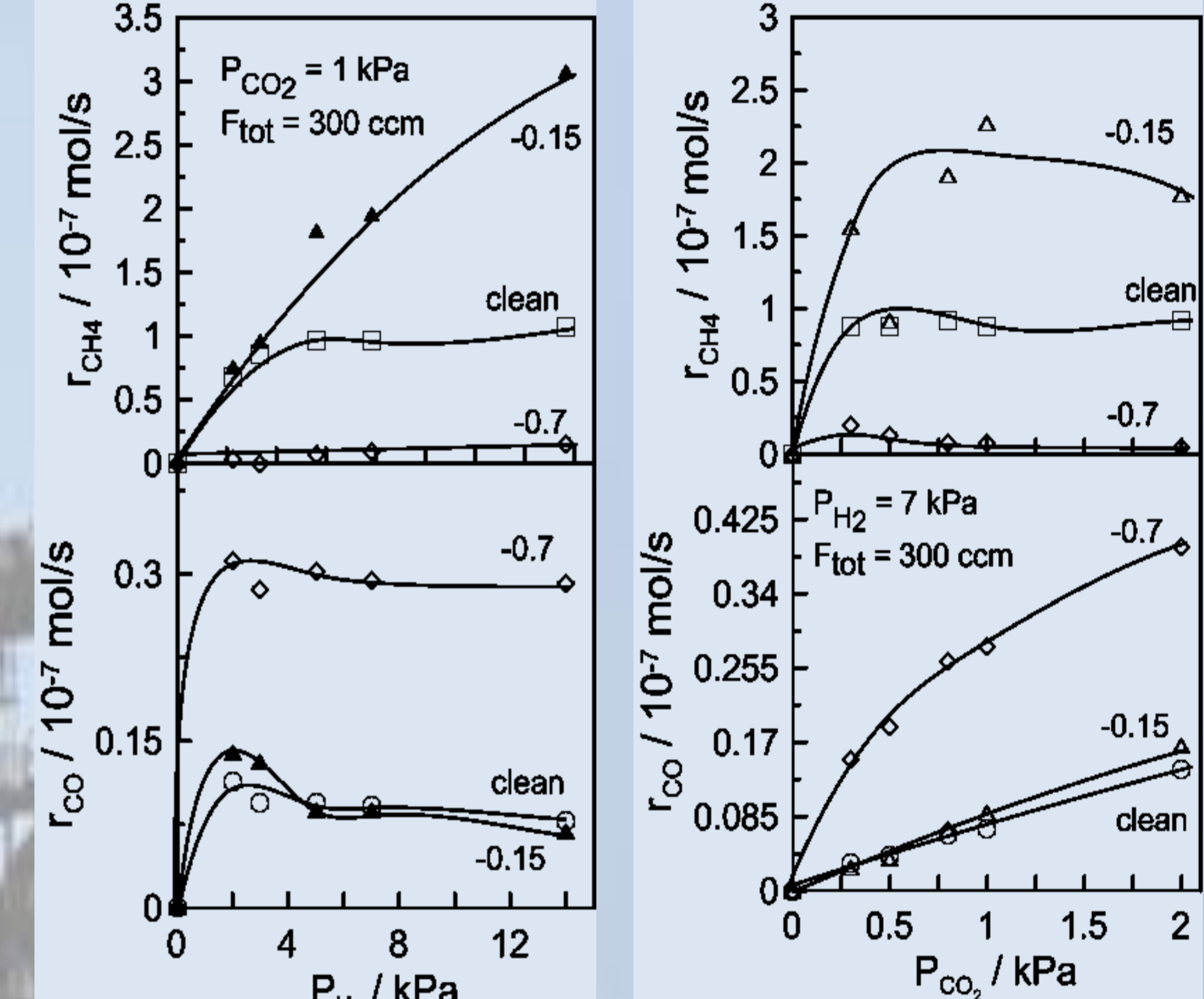
Ru/YSZ
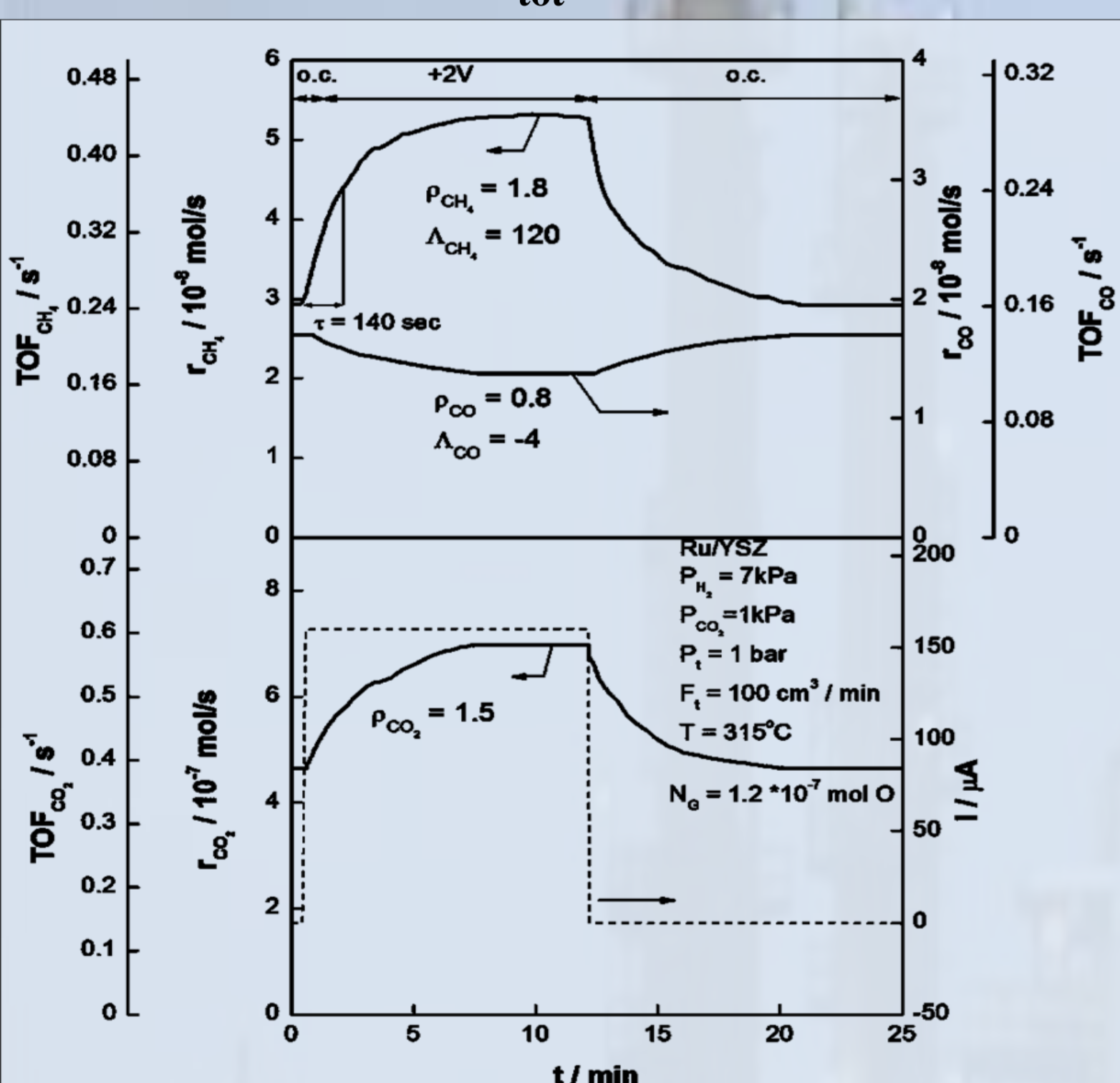
Ru/ β''- Na⁺-Al₂O₃

Ru/ β''- K⁺-Al₂O₃

In all cases, the rate of methanation reaction is positive order in H_2 and zero or negative order in CO_2 while the rate of CO is negative order in H_2 and positive order in CO_2. Thus, according to the promotional rules of EPOC [1], electrophobic behavior ($\partial r/\partial U_{WR} > 0$) is expected for the mathane production and electrophilic for the RWGS ($\partial r/\partial U_{WR} < 0$).
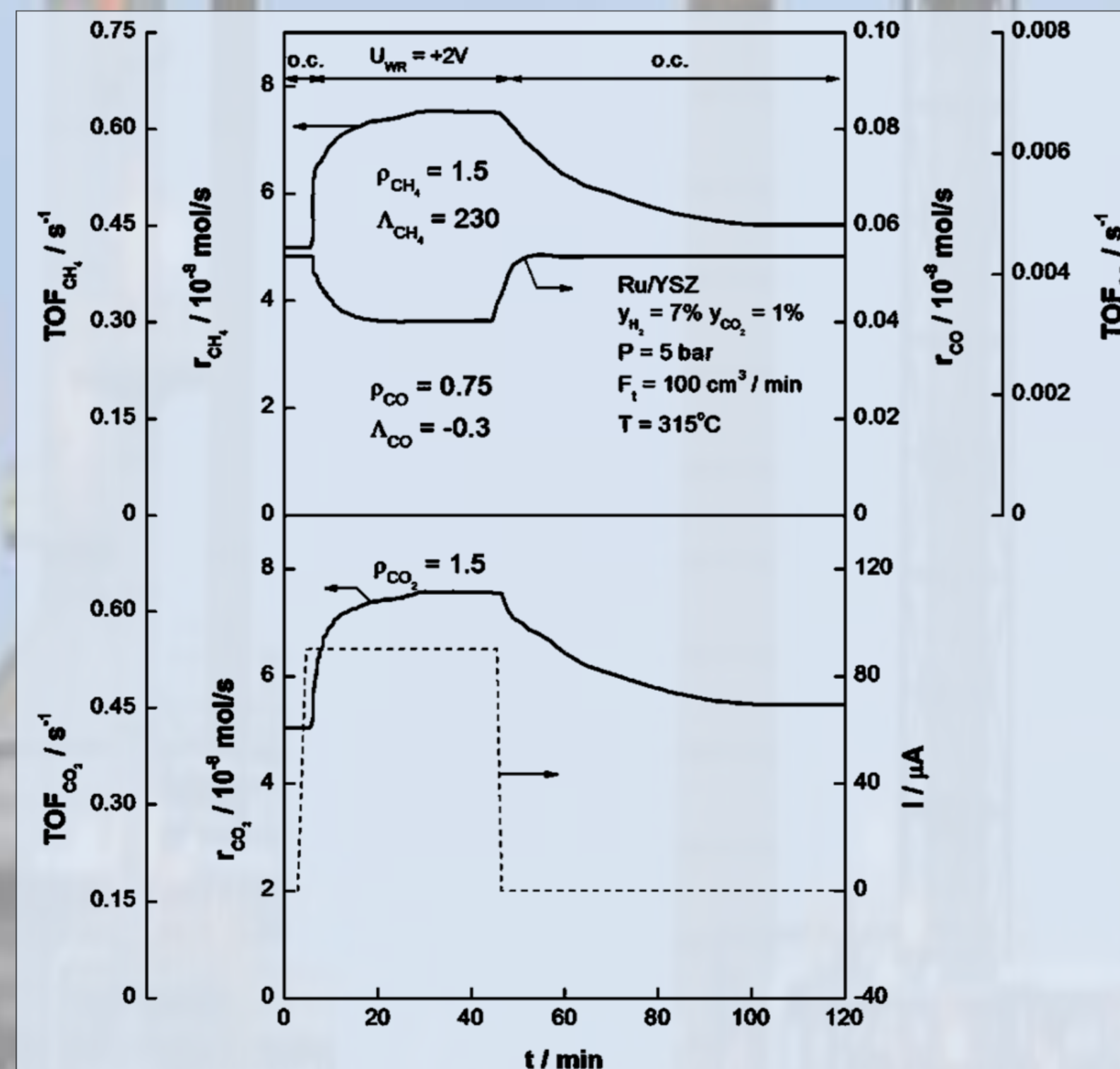
Transient effect of a constant applied current on the rates of CH_4 and CO formation and on the catalyst potential U_{WR} . $P_{H2}/P_{CO2} = 7$, $T = 320°C$
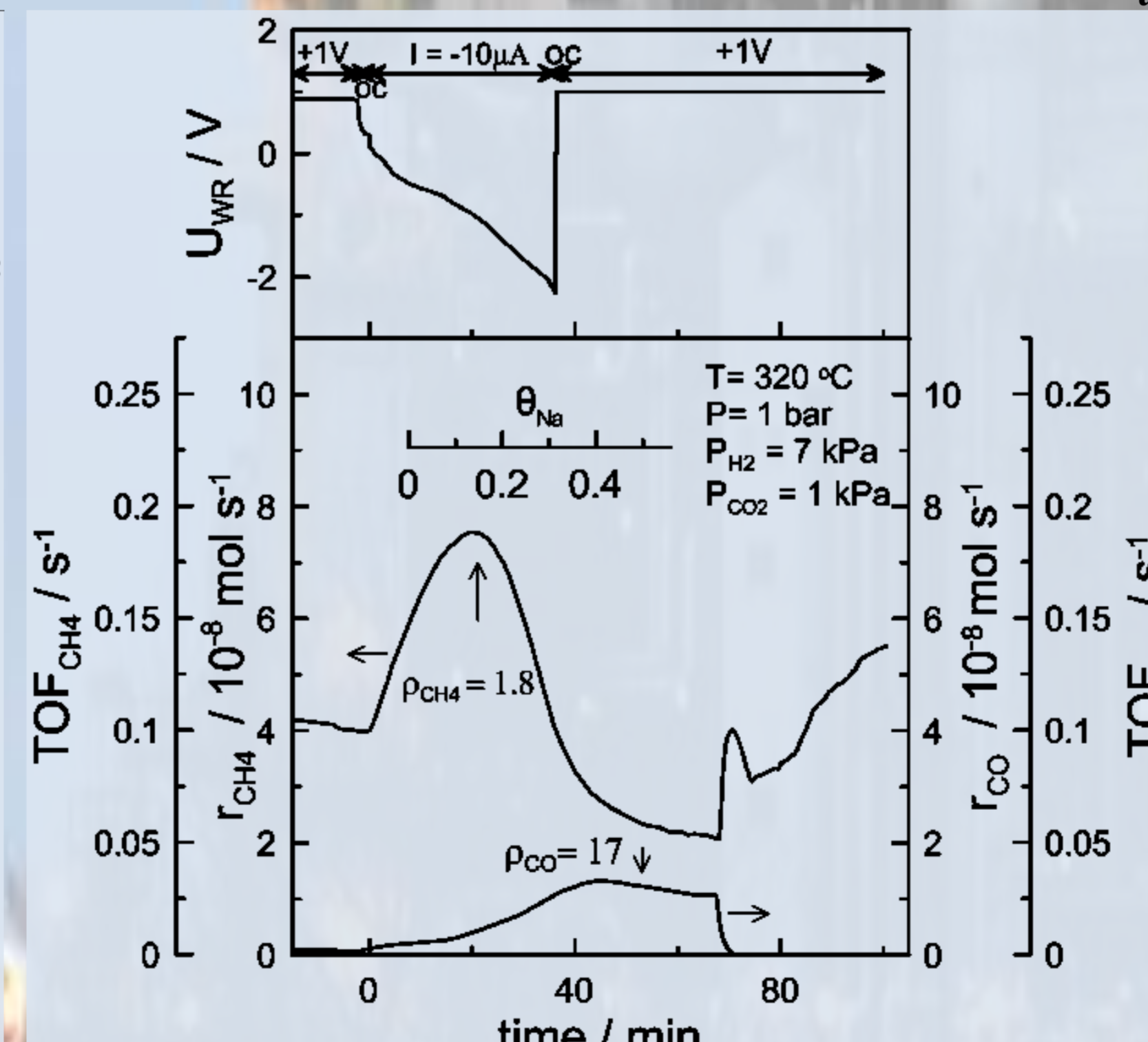
Ru/YSZ

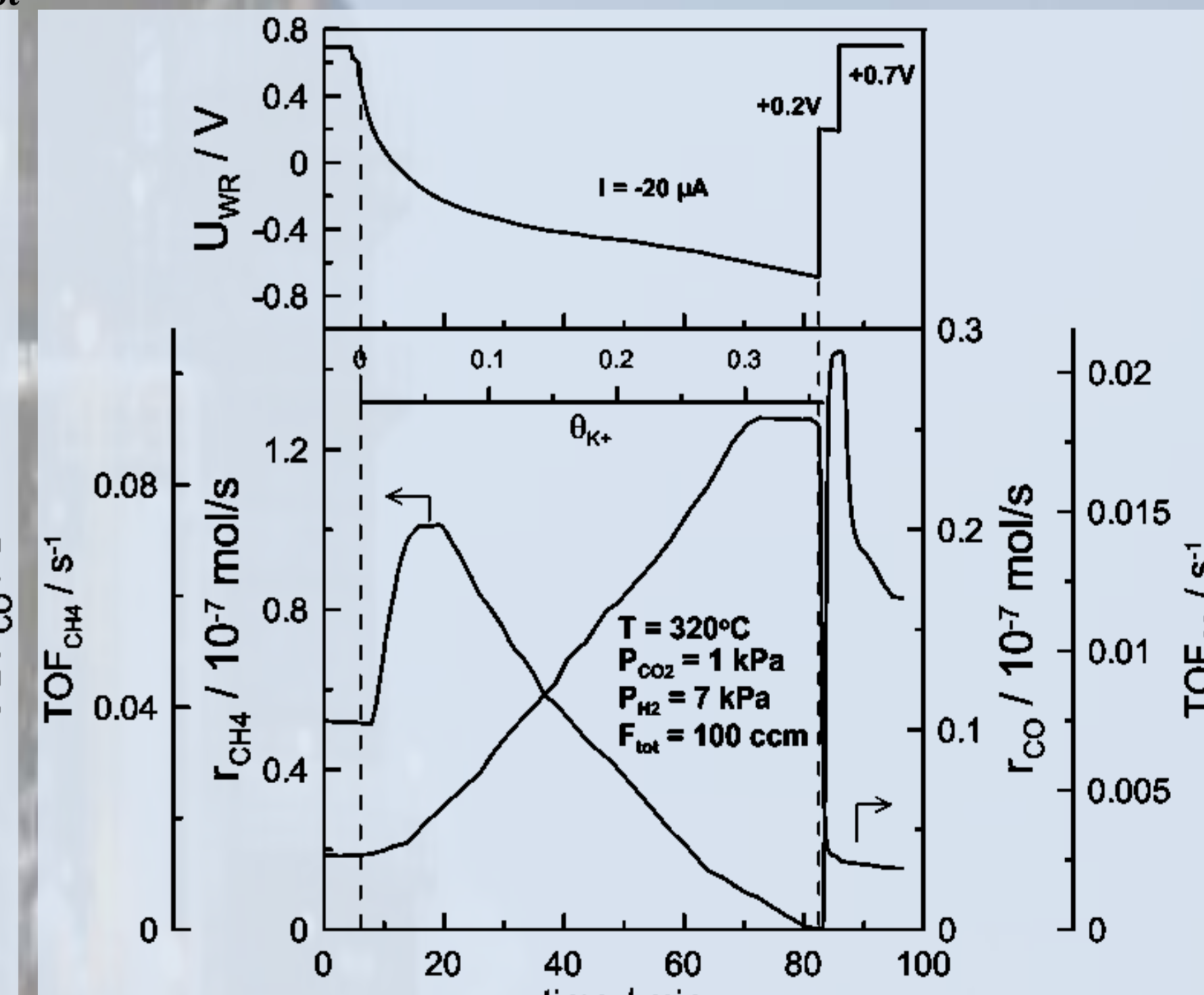$P_{tot} = 1$ bar

$P_{tot} = 5$ bar

Ru/β''-Na⁺-Al₂O₃

$P_{tot} = 1$ bar

Ru/β''-K⁺-Al₂O₃

Ru/YSZ: Positive potential application that is, O^{2-} supply to the catalyst surface, causes a 50% increase in the rate of CH_4 formation (electrophobic bahavior) and a 25% decrease in the rate of CO formation (electrophilic behavior). Negative potential application (-2V) results in the opposite behavior [3].

Ru/β''-Al₂O₃: In the case of β''-Al_2O_3 again the rate of methane exhibits an electrophobic behavior, and the rate of CO an electrophilic one. Thus, by the application of a negative current, there is an increase on the rate of CO and a decrease on the rate of CH_4. However, at small coverages of Na^+ and K^+, the rate of CH_4 is enhanced, passing through a maximum. This can be attributed to the kinetics in H_2 and CO_2.

Conclusions

✓CH_4 production is enhanced by applying electronegative promoter.
✓Negative potential and electropositive promoters favor CO formation.
✓In the case of β''-Al_2O_3, Na^+ and K^+ can promote the methanation reaction for coverages up to 20% and 5% respectively, due to enhanced CO_2 chemisorption.
✓In all cases, the results are in agreement with the predictions of the promotional rules based on the reactions kinetics.

References

[1] I. Omae, Catal. Today 115 (2006) 33-52.
[2] C.G. Vayenas et al., *Electrochemical Activation of Catalysis*, Kluver Academic/Plenum Plublishers, NY, 2001.
[3] D. Theleritis, S. Souentie, A. Katsaounis and C.G. Vayenas, ACS Catalysis 2 (2012) 770-780.
[4] D. Theleritis, M. Makri, S. Souentie, A. Caravaca, A. Katsaounis and C.G. Vayenas,ChemElectroChem 1 (2014) 254- 262.

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