

Mechanistic kinetic study of CO₂ methanation in the presence of a Ru/Al₂O₃ catalyst

Leonardo Falbo¹, Alessandro Porta¹, Carlo Giorgio Visconti^{1*}, Luca Lietti¹,
Claudia Bassano², Paolo Deiana²

¹ Politecnico di Milano, Milano 20156 (Italy); ² ENEA, S. Maria di Galeria, Rome 00123 (Italy)

*carlo.visconti@polimi.it

Highlights

- Low-loading supported Ru catalysts are promising for once-through CO₂ methanation
- A new empirical rate law well describes CO₂ conversion over a wide range of conditions
- A mechanistic kinetic model is proposed to describe CO₂ conversion and CH₄ selectivity

1. Introduction

Carbon dioxide is the most abundant greenhouse gas released by human activities and its utilization as a C1 building block is industrially and environmentally attractive. Among the proposed CO₂ (re)utilization technologies, CO₂ hydrogenation to SNG (Substitute Natural Gas) is particularly interesting because it produces a fuel with a wide market and easily transportable with the existing infrastructures. In addition, when using renewable H₂ produced by H₂O electrolysis, SNG production becomes also a route (Power-to-Gas, PtG) for the chemical storage of excess renewable/nuclear electric energy which is wasted today [1].

The highly exothermic CO₂ methanation is limited by thermodynamic constraints at high temperatures, where conventional Ni-based catalysts are employed. At these conditions, CO selectivity is also rather high and the catalyst stability with time is poor. In this regard, Ru-based catalysts are of interest for the process intensification because are active at lower temperatures, allowing higher CO₂ per-pass conversion with a selectivity to CH₄ over 99% for a long period of time [2].

The goal of this work is the kinetic description of CO₂ methanation over a Ru-based catalyst under process conditions of interest for the PtG technology. For this purpose, a commercial catalyst has been tested over a wide range of process conditions, working at high CO₂ conversions and with concentrated CO₂/H₂ streams to investigate at best conditions of industrial interest. The collected data have been fitted using both CO₂ conversion and CH₄ formation rate equations.

2. Methods

A 0.5 wt.% Ru/Al₂O₃ commercial catalyst (206199, Aldrich) was tested in a lab-scale rig operating 24/7, equipped with a tubular reactor and an on-line GC. Before the activity tests, the catalyst (sieved and ground so that $d_p < 106 \mu\text{m}$) was reduced in situ with H₂ at 400 °C for 3 h. Then, the effects of T, P, GHSV, H₂/CO₂, P⁰_{N₂} and P⁰_{H₂O} were investigated in the range 250-410 °C, 1-7 ata, 3.75-10 L(STP)/h/g_{cat}, 1-5 mol_{H₂}/mol_{CO₂}, 0-0.4 ata and 0-0.3 ata, respectively. Concerning kinetic modeling, developed rate equations were integrated in an isothermal homogeneous plug-flow reactor model. Both mass and heat transfer limitations were assessed with experimental and empirical criteria, in order to collect data under kinetic control. Kinetic parameters were estimated by fitting the experimental data, performing a nonlinear regression based on the least-square method.

3. Results and discussion

Among the empirical kinetic expressions present in the literature for CO₂ methanation, the formulation proposed by Lunde and Kester [2] (green line, Figure 1) is the only one able to reasonably describe the CO₂ conversion in a wide range of process conditions. Such a model, however, tends to overestimate CO₂ conversion at high pressure. Accordingly, we suggest here a modified rate expression, explicitly accounting for the negative dependence of CO₂ conversion rate on the partial pressure of water in the reactor, further improving the model capability to describe CO₂ conversion (red line, Figure 1).

To overcome the limits of the empirical rate expression, based on evidences collected by operando IR study of our catalyst and following the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach, we have developed different mechanistic rate expressions for CO₂ consumption. Each expression has been derived by setting a rate determining step (RDS) and under the hypothesis of the existence of a most abundant surface intermediate (MASI). Figure 1 shows the performance of the LHHW model providing the best match with the experimental data (orange line, Figure 1).

Finally, in order to develop a kinetic model able to describe the (very low) CO selectivity of our catalyst, an additional mechanistic model was developed using the LHHW approach, which also accounts for the possibility of adsorbed CO (the key reaction intermediate) to be desorbed. Notably, the resulting kinetic model shows a very good fitting of experimental data (blue line, Figure 1) both in terms of CO₂ conversion and in terms of CH₄ selectivity, with physically and thermodynamically consistent kinetic parameters.

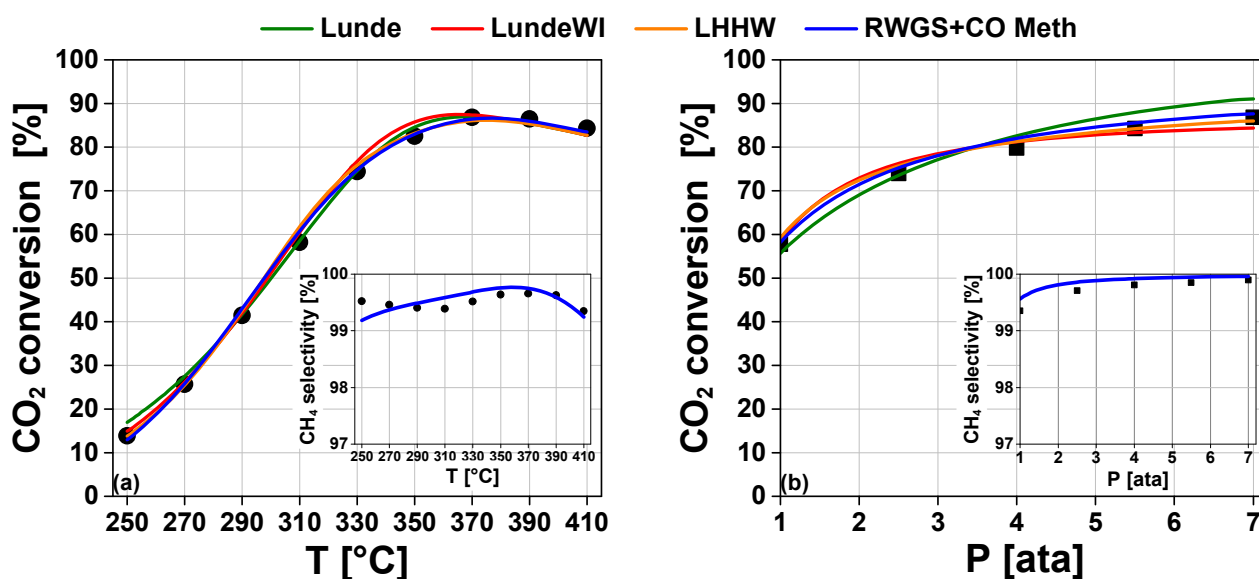


Figure 1. Effects of (a) temperature and (b) pressure on CO₂ conversion and (inset) CH₄ selectivity. Experimental data (symbols) compared to model predictions (full lines).

4. Conclusions

Our work shows that simple power law equations can accurately describe the CO₂ conversion rate over Ru/Al₂O₃ catalysts. Even better fittings, however, can be obtained using mechanistic models developed on the basis of spectroscopic evidences. Also, these evidences can be used to develop a detailed kinetic model able to predict both the CO₂ consumption and the CH₄ formation rate at the same time. Such a model represents a key-tool for the design and the simulation of industrial methanation reactors and PtG processes.

References

- [1] C. Janke, M. Duyar, M. Hoskins, R. Farrauto, Appl. Catal. B: Environ. 184 (2014) 152
- [2] P.J. Lunde, F.L. Kester, J. Catal. 30 (1973) 423

Keywords

Power to Gas, Ru-based catalyst, CO₂ methanation, kinetic modeling.