CO_2 hydrogenation to CH_4

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1. Objectives

- To familiarize with a plug flow catalytic reactor for gas phase reactions at elevated temperatures (200-500°C)
- To be able to summarize and analyze catalytic testing data in the form of tables and graphs
- To study the catalytic conversion and selectivity of CO_2 to CH_4 as a function of temperature over heterogeneous catalysts
- To compare the catalytic activity of different catalysts (Ru/Al_2O_3, Ni/Al_2O_3)
- To evaluate the influence of the nature and loading of the metal

2. Background

In recent years, many solutions have been proposed to reduce the carbon dioxide footprint of industry, transportation, and energy conversion. Considerable attention has been focused on carbon dioxide storage by exploiting new solutions for carbon capture but also the transformation of carbon dioxide to renewable fuels such as methanol, liquid hydrocarbons, and methane [1]. Besides being the main component of natural gas, methane can be produced by microbiological processes as well as by thermochemical routes using heterogeneous catalysis.

The anaerobic digestion of biomass produces biogas, which consists of methane and significant amounts of carbon dioxide. Hence, the implementation of a downstream process that converts the undesired carbon dioxide to additional methane is desirable. In this context, the catalytic hydrogenation of carbon dioxide to methane has been widely studied, which is known as the Sabatier reaction (eq. 1). It is thermodynamically favorable but has significant kinetic limitations since the reduction of the fully oxidized carbon to methane is an eight-electron transfer process [1]. Hence, the reaction requires a catalyst to achieve acceptable rates and selectivities.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H°_{298} = -165.12\ kJ/mol \qquad \text{(Eq. 1)}$$

Depending on the catalyst used and the reaction conditions, carbon monoxide can also be formed via the reverse water gas shift reaction (eq. 2). Carbon monoxide can then be further reduced by hydrogen to produce methane (eq. 3) [2].

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H°_{298}$= +41.16 kJ/mol (Eq. 2)

$CO + 3H_2 \rightarrow CH_4 + H_2O$ $\Delta H°_{298}$= -206.28 kJ/mol (Eq. 3)

A wide range of catalysts has been investigated to improve both reaction rate and selectivity. The main metals studied are the group VIII metals (e.g., Ru, Rh, Ni) and other noble metals (e.g., Pd, Pt) [1]. Catalyst degradation at high temperatures mainly through sintering and the limited catalyst stability over time due to the presence of poisoning species such as sulfur in the reaction gas feed are the major challenges. Hence, scientists aim at minimizing these limitations by the appropriate choice of the catalyst type (active metal, oxide supports, metal loadings, etc.)

3. Methods and materials

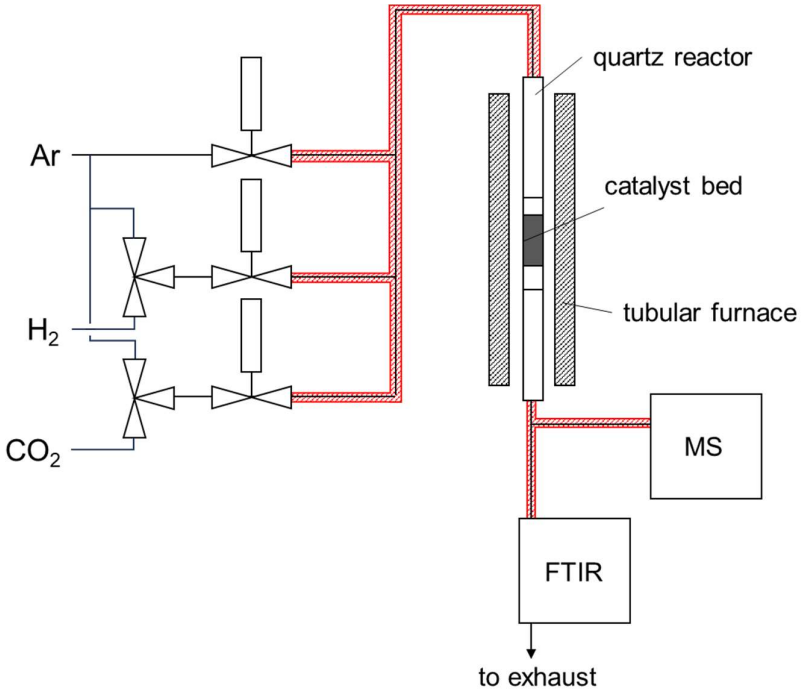

Figure 1. Scheme of the CO_2 hydrogenation setup.

Figure 2. Plug flow reactor to study catalysts in powder form.

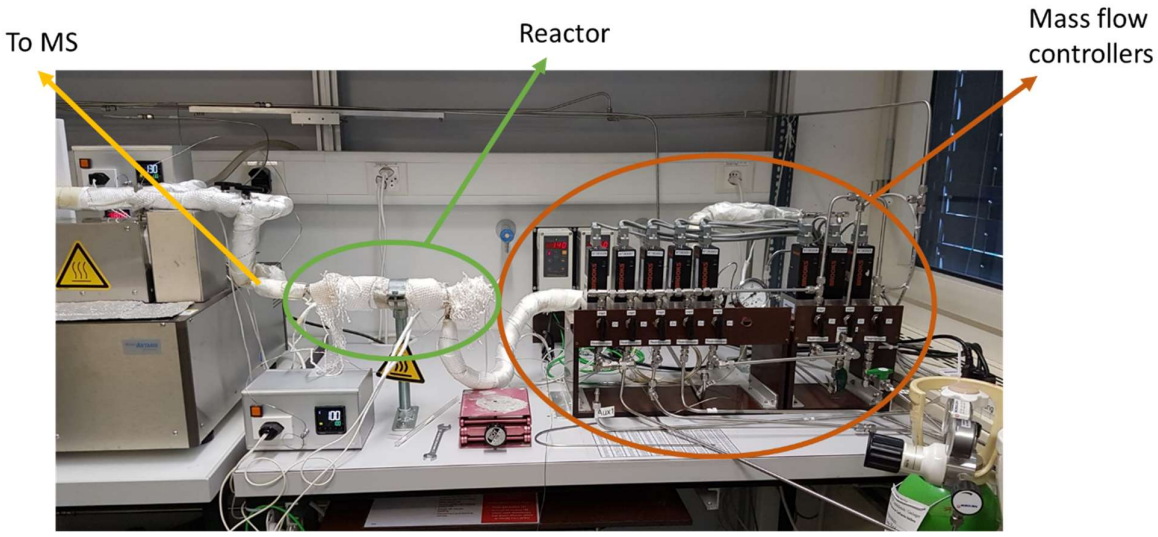

Figure 3. CO_2 hydrogenation setup.

The catalyst bed is positioned in a quartz reactor (Figure 2) mounted in a tubular furnace (Figure 3). A temperature sensor is placed in the reactor and the sensor tip is inserted in the catalyst bed. This allows to record the catalyst temperature throughout the experiment. Mass flow controllers (MFCs) together with a LabVIEW interface are used to control the gas flow rates and prepare gas blends. Water is generated in situ from precise flows of hydrogen and oxygen through an oxidation catalyst. Since water is fed to the catalyst, the entire setup is heated up to avoid water condensation in the gas lines and the reactor. The lines are heated using heating wires and are then isolated using insulation bands (in white in Figure 3). Finally, the composition of the reactor exhaust is analyzed by a mass spectrometer (MS, Figure 1) and Fourier transform infrared spectrometer (FTIR).

The reaction mixture is composed of 3 vol% CO_2 (from pure CO_2) and 12 vol% H_2 (from pure H_2), the rest being Ar. The total flow for the experiment is 50 mL/min at STP (0°C at 1 atm).

You will follow the MS signals (m/z) indicated below.

MS signal (m/z)	gas component
2	H_2
15	CH_4
18	H_2O
28	CO, CO_2, N_2
32	O_2
40	Ar
44	CO_2

4. Experimental procedure

1. You will analyze three samples, 5 wt% Ru/Al_2O_3, 5 wt% Ni/Al_2O_3 and 10 wt% Ni/Al_2O_3.
2. Load the catalyst in the reactor (50 mg + 50 mg of cordierite for dilution, both provided) between two layers of quartz wool. Cordierite is used to obtain an even dispersion of the catalyst and to avoid temperature hot spots.
3. Prepare a reduction feed containing 12 vol% H_2 in Ar (50 mL/min). Determine the flow rate of H_2 and Ar for a total of 50 ml/min and change setpoint values in LabView.
4. Pre-reduce the catalyst. A pre-treatment allows desorbing possible impurities and water from the catalyst. It also ensures that all your experiments are carried out with the same starting material (i.e. oxidation state, particle size, etc.) which makes the comparison between experiments more accurate.
5. Heat the reactor to 500°C (20°C/min) and leave it at this temperature for 30 min.
   Aim: to activate and to stabilize the catalyst.
6. Cool to 200°C (20°C/min).
7. Change to reactor by-pass.
8. Add CO_2 to the feed so to reach a composition of the feed of 12 vol% H_2 and 3 vol% CO_2 (H_2:CO_2= 4), rest Ar. Determine the flow rate of CO_2, H_2 and Ar for a total of 50 ml/min and change setpoint values in LabView.
   Aim: to obtain a stable flow before starting heating the catalyst in the reactor under this feed, to obtain the MS signal of CO_2 and H_2 at known concentrations. This provides better accuracy for the determination of the amount of CO_2 and H_2 consumed during the reaction.
9. Change to reactor and wait signals to stabilize (ca. 15 min).
10. Test the catalytic activity as a function of the reaction temperature:
    - increase the reactor temperature to 500°C (5°C/min).
    - Dwell at 500°C for 10 min.

- Decrease the reactor temperature to 200°C (5°C/min).
- Dwell at 200°C for 10 min.

11. Change to reactor by-pass and analyze the inlet flow again for ca 10 min
    Aim: to obtain a MS signals of all gas phase components at a known concentration and to determine their concentration during reaction to be able to determine conversion.

6. Report

1. CO_2 concentration can be best measured by MS. Online FTIR delivers already the concentration values of CH_4 and CO.
2. Plot the CO_2 conversion (%), CH_4 selectivity (%), and CO selectivity (%) as a function of temperature (up and down temperature ramp on the same graph) that you determine using the following equations:

$$\text{conversion of i [\%]} = \frac{\text{conc}_{i,\,t=0} - \text{conc}_{i,\,t}}{\text{conc}_{i,\,t=0}} * 100$$

$$\text{selectivity of i towards x [\%]} = \frac{\text{conc}_{x,\,t} - \text{conc}_{x,\,t=0}}{\text{conc}_{i,\,t=0} - \text{conc}_{i,\,t}} * 100$$

3. Discuss the results; describe and explain what you observe in the graph.
4. Compare your results with those obtained using the other catalyst samples that have been measured by the other groups. Among these catalysts, which one would you choose for operation at an industrial scale? Explain your answer.
5. How would you explain the difference in activity observed between the two catalysts with low metal content (Ru/Al_2O_3 and Ni/Al_2O_3)?
6. Compare the temperature ramps (5°C/min) performed with the three catalysts with that of the empty reactor and discuss what you observe.
7. For your report you will receive three files for each sample (temperature ramp, MS data, FTIR data) and one file relative to the temperature ramp of the empty reactor.

7. References

[1] W. Wang, J. Gong, *Methanation of carbon dioxide: an overview*, Front. Chem. Sci. Eng. 5 (2011) 2.

[2] G. Garbarino, P. Riani, L. Magistri, G. Busca, *A study of the methanation of carbon dioxide on Ni/Al_2O_3 catalysts at atmospheric pressure*, Int. J. Hydr. En. 39 (2014) 11557.