RE6 - Kinetics: Heterogeneous Catalyzed Reaction

Methanation of CO_2 over a Ru/Al_2O_3 catalyst

Supervisor: Ask Lysne*

Abstract

The CO_2 methanation reaction will be investigated at different reaction conditions over a Ru-based catalyst. The experiment is conducted in a fixed bed quartz reactor at atmospheric pressure and temperatures of 350-370 °C in H_2-rich conditions. The reactant gas stream will contain CO_2 and H_2 diluted with He and N_2 (internal standard). The effluent gas flow will be analyzed using micro gas chromatography (micro-GC). Calibration curves for mass-flow controllers (MFCs) are found based on provided calibration data. A simple three-level micro-GC calibration is performed.

The reaction order for CO_2 (assuming a power-law rate model) will be determined by changing the CO_2 partial pressure. The activation energy will be determined based on the Arrhenius equation by varying the reactor temperature.

* PhD student, Department of Chemical Engineering, NTNU
  Mail: ask.lysne@ntnu.no
  Phone: 97006222

1. Theory

1.1. Reaction Kinetics

The conversion of CO_2 and H_2 to CH_4 is described by the exothermic reaction (1) and occurs on solid catalysts containing Co, Ni, Fe or Ru. The methanation of CO_2 including green H_2 (from water hydrolysis with electricity from renewable energy sources) has been proposed for sustainable CH_4 production as part of a future *carbon capture and utilization* (CCU) scheme. At relevant conditions possible side reactions may include the endothermic *reverse water gas shift* (RWGS) reaction (2).

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H^0_{298K} = -164 \; kJ/mol \qquad (1)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^0_{298K} = 41 \; kJ/mol \qquad (2)$$

At low conversion levels, the kinetics of reaction (1) can be described by the power-law rate expression shown in equation (3). Here $-r_{CO_2}$ is the rate of CO_2 consumption, k is the rate constant, p is the partial pressure of the reactants and a and b are the reaction order for CO_2 and H_2 respectively. In a H_2-rich atmosphere, the reaction rate can be considered independent of H_2 partial pressure ($b = 0$), and equation (3) is reduced to equation (4).

$$-r_{CO_2} = k p_{CO_2}^a p_{H_2}^b \qquad (3)$$

$$-r_{CO_2} = k p_{CO_2}^a \qquad (4)$$

At differential reactor conditions, the reaction rate is related to the conversion level by equation (5). Here $F^0_{CO_2}$ is the molar flow rate of CO_2 at the reactor inlet, X_{CO_2} is the CO_2 conversion and ΔW is the applied catalyst mass. The differential reactor assumption requires the conversion level to be sufficiently low such that the CO_2 partial pressure can be considered constant throughout the reactor. If the overall conversion is too high the changing CO_2 partial pressure through the reactor has to be taken into account with an integral reactor model (not required in this experiment).

$$-r_{CO_2} = \frac{F^0_{CO_2} X_{CO_2}}{\Delta W} \qquad (5)$$

The CO_2 reaction order a can further be determined as the slope of the linearized equation (4) shown in equation (6). Plotting $\ln\left(-r_{CO_2}\right)$ as a function of $\ln(p_{CO_2})$ at different CO_2 partial pressures should hereby give a straight line from which the slope can be found by linear regression analysis. This requires $\ln(k)$ and hereby the reaction temperature to be kept constant.

$$\ln\left(-r_{CO_2}\right) = \ln(k) + a \cdot \ln\left(p_{CO_2}\right) \qquad (6)$$

The rate constant k is related to the reaction temperature by the Arrhenius equation (7). Here A is the constant pre-exponential factor, R is the universal gas constant and T is the reaction temperature. The activation energy E_a can be determined by linearization of equation (7) as shown in equation (8).

$$k = Ae^{-\frac{E_a}{RT}} \tag{7}$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{8}$$

Plotting $\ln(k)$ as a function of $1/T$ at different reaction temperatures should here give a straight line with $-E_a/R$ as the slope and $\ln(A)$ as the y-axis interception. The rate constant k can here be determined by equation (4) at each reaction temperature.

1.2. Gas Chromatography

Gas chromatography (GC) is a separation process commonly applied for the analysis of gas samples. In combination with a suitable detector, the technique can provide identification and quantification of compounds in complex mixtures. The analytes are separated by partitioning between a mobile and stationary phase. The mobile phase consists of an inert carrier gas into which the sample is injected. The stationary phase is a high surface area solid or liquid phase, packed into or coated onto the GC column. The different sample compounds are adsorbed onto or absorbed into the solid or liquid phase and separated based on their different affinities for the stationary phase. The components are consecutively eluted from the column at different times (called retention time) and can hereby be individually quantified. Complete separation of the compounds within the sample is achieved by adjusting micro-GC parameters like column temperature and pressure.

The micro-GC is a high-speed GC system designed for rapid analysis of gas mixtures. Such systems typically apply long wall-coated capillary columns and a high carrier gas flows to achieve fast and efficient separation. The *thermal conductivity detector* (TCD) is a commonly applied micro-GC detector measuring changes in the thermal conductivity of the gas flow effluent from the GC column relative to a reference carrier gas flow.

In order to function as a qualitative and quantitative analysis tool, the GC apparatus needs to be calibrated with relevant gasses. This is done by analyzing gas mixtures with known compositions to identify the retention time and response factor for each component. The response factor RF_i for compound i is defined by equation (9). Here A_i is the peak integration area (from the chromatogram) and x_i is the molar fraction.

$$RF_i = \frac{A_i}{x_i} \tag{9}$$

One calibration method is the internal standard method. An inert gas (N_2 in this experiment) present in known amounts in all measurements here serves as the internal standard. The amounts of all other components are further determined relative to the amount of the internal standard. A relative response factor RRF_i is here introduced defined by equation (10).

$$RRF_i = \frac{RF_i}{RF_{IS}} \tag{10}$$

Here RF_{IS} is the response factor for the internal standard. Insertion of equation (9) into equation (10) gives equation (11), where A_{IS} and x_{IS} are the peak area and molar fraction for the internal standard.

$$RRF_i = \frac{A_i}{x_i} \cdot \frac{x_{IS}}{A_{IS}} \tag{11}$$

The molar flows F_i and F_{IS} can further be introduced as shown in equation (12), where F_{tot} is the total molar flow. Rearranging equation (12) gives the final equation (13) showing how F_i in the product gas stream can be determined from measuring A_i and A_{IS} when F_{IS} and RRF_i are known.

$$RRF_i = \frac{A_i}{A_{IS}} \cdot \frac{x_{IS}}{x_i} \cdot \frac{F_{tot}}{F_{tot}} = \frac{A_i}{A_{IS}} \cdot \frac{F_{IS}}{F_i} \tag{12}$$

$$F_i = \frac{A_i}{A_{IS}} \cdot \frac{F_{IS}}{RRF_i} \tag{13}$$

The RRF_i can be determined from equation (13) by plotting $A_i F_{IS}/A_{IS}$ as a function of different molar flows F_i during GC calibration. This should afford a straight line with RRF_i as the slope. The molar flows are calculated from the volumetric flows following ideal gas law.

2. Experimental

2.1. Experimental Preparations

The kinetic experiment will be performed in a catalyst testing apparatus with the simplified flow sheet shown in **Figure 2.1.1**. The product gas flow is analyzed with an Agilent Technologies 490 Micro-GC equipped with a CP-COX column and a TCD detector. The micro-GC method parameters are listed in **Appendix A.1**. The reactor is loaded with the Ru/Al$_2$O$_3$ catalyst (300 mg) containing 2 wt% Ru on a γ-Al$_2$O$_3$ support. The catalyst bed is diluted with inert SiC (700 mg) to ensure isothermal conditions. A plug of quartz wool is placed below and above the bed to keep the catalyst in place. The reactor is closed and placed inside the heating furnace (oven) and the gas feed and outlet lines are connected. The thermocouple is placed inside the thermocouple holder in the reactor center to properly monitor the reaction temperature.

All *mass-flow controllers* (MFCs) used in this experiment are manually operated, and the MFC setpoint is an analog signal in percentage and not the flow directly. All MFCs have been calibrated and the calibration data is found in **Appendix A.2**. This data is applied to afford the MFC calibration curves, meaning the volumetric flow in mL/min (at standard conditions, 1 atm and 0 °C) as a function of MFC setpoint, by linear regression analysis.

The reactor is first leak tested with N$_2$ using a leak detection spray and secondly with H$_2$ using a flammable gas detector. The system is purged with N$_2$ (minimum 100 mL/min) for 15 min through the

reactor and 15 min through the reactor bypass to remove air from the system before H_2 introduction. The heating furnace is isolated, and the condenser cooling water is switched on. The latter is very important to protect the GC from any H_2O formed thorough reaction (1) and (2).
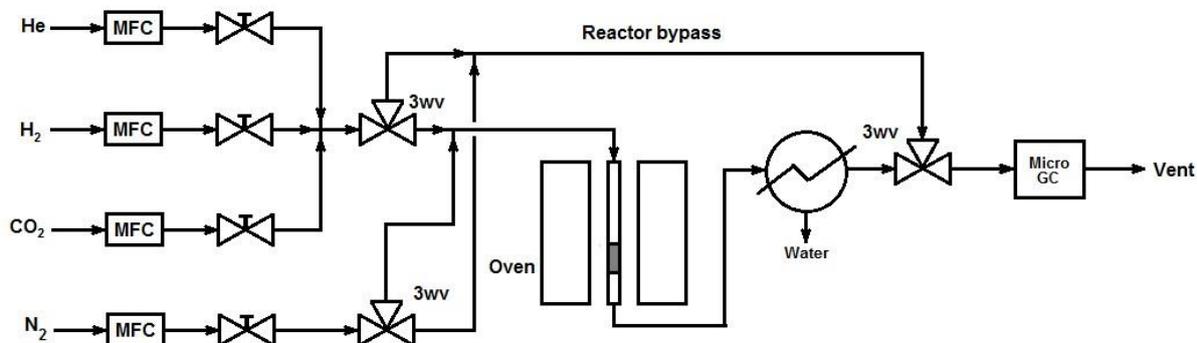

Figure 2.1.1: *Simplified flow sheet of the catalyst testing apparatus with mass-flow controllers (MFC), three-way valves (3wv) and gas chromatograph (GC).*

2.2. Retention Times and Micro-GC Calibration

After leak testing, the three-way valves are set to direct the flow through the reactor bypass. The feed gases (He, N_2, H_2 and CO_2) are further introduced one by one while analyzing the flow with the micro-GC to identify the peak position of each component in the chromatogram. The retention time (defined as the time of the peak maximum) for each compound is hereby determined.

A three-level calibration of the micro-GC is performed with the conditions shown in **Table 2.2.1**. The relative response factor of CO_2 with respect to the internal standard N_2 is hereby determined following the procedure described in **Section 1.2**. It is important to wait for the flows to stabilize at each set of conditions. Three measurements should be included at each calibration level.

Table 2.2.1: *Applied conditions for micro-GC calibration.*

Calibration Level	Volume Fraction [vol%] (a)				Total Flow [mL/min] (a)
	CO_2	H_2	N_2	He	
1	5	60	15	20	200
2	7.5	60	15	17.5	200
3	10	60	15	15	200

(a) At standard conditions (1 atm and 0 °C).

2.3. Catalyst Pretreatment

After GC calibration, the three-way valves are set to direct the flow through the reactor. When stored in air, the Ru catalyst is partly or fully oxidized. In the CO_2 methanation reaction, Ru is catalytically active only in the reduced metallic state. It is hereby necessary to reduce the catalyst before the experiment. The Ru reduction reaction is shown in equation (14).

4

$$RuO_2 \ (s) + 2H_2 \ (g) \rightarrow \mathrm{Ru} \ (s) + 2H_2O \ (g) \tag{14}$$
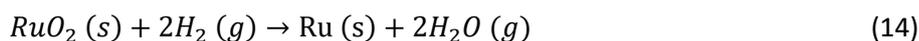
The reduction is performed in a flow of 50 vol% H_2 in N_2 (total flow of 200 mL/min) while heating the catalyst bed from room temperature to 350 °C with a heating rate of 10 °C/min. After setting the H_2 and N_2 flows, the heating furnace is turned on with an automated temperature program (prepared by the supervisor) including the reduction temperature ramp.

2.4. Kinetic Experiment

The reaction conditions applied during the 5 steps of the complete experiment is shown in **Table 2.4.1**. The experiment consists of 2 parts, where the CO_2 reaction order is determined in part 1 (step 1-3) and the activation energy of the reaction in part 2 (step 3-5).

Table 2.4.1: *Applied reaction conditions for the kinetic experiment.*

Step	Volume Fraction [vol%] (a)				Total Flow [mL/min] (a)	Temperature [°C]
	CO_2	H_2	N_2	He		
1	5	60	15	20	200	350
2	7.5	60	15	17.5	200	350
3	10	60	15	15	200	350
4	10	60	15	15	200	360
5	10	60	15	15	200	370

(a) At standard conditions (1 atm and 0 °C).

After catalyst reduction (when the temperature reaches 350 °C), the automated temperature program dwells for 45 min at each experimental step in **Table 2.4.1**. The H_2, N_2 and He flows should be adjusted first before introducing CO_2 to the system. The micro-GC is set to analyze the product gas composition continuously. It is important to keep track of time to adjust the reaction conditions (MFC setpoints) every 45 min. The heating rate between step 3-5 is set to 10 °C/min. Note that only the data acquired at steady-state conditions (towards the end of each step) should be included in the calculations. At least three measurements are included at each step.

Upon completion of step 5, the automated temperature program will cool down to room temperature with a heating rate of 10 °C/min. The micro-GC analysis is now stopped and the CO_2, H_2 and He flows are closed. The system is purged with N_2 (100 mL/min) during the cool-down. The cooling water is left on until the system has reached room temperature. The reactor is cleaned by the supervisor.

Appendix

A.1. Pre-Experimental

Before performing the experiment, the students should carefully read the experiment description and risk assessment and prepare the work plan. The work plan should include a checklist with all the tasks to do in the lab. Make sure to shortly include:

- The main goals and objectives for the experiment.
- Any required personal protective equipment (and why it is required).
- The purpose of each step in the procedure.
- How the data will be used (what information you will get) from each step (or series of steps).
- How the GC raw data can be converted to molar flow rates and how to determine the CO_2 conversion, reaction rate, reaction order and the activation energy. Make sure to mention any applied assumptions.
- The completed **Table A.5.1** overview of applied conditions in **Appendix A.5** with the required MFC setpoints and volumetric feed flows. The MFC setpoints are determined from the MFC calibration curves based on the calibration data provided in **Appendix A.4**.

The work plan must be delivered digitally to the supervisor <u>minimum 3 working days</u> before the lab day. You are advised to deliver the work plan at your earliest convenience, since it has to be approved by the supervisor before you are allowed to conduct the experiment.

A.2. Report Guidelines

The report should include the following sections:

- **Introduction:** Provides a clear outline of the experimental objectives. The necessary theoretical background should be briefly described.
- **Experimental:** The experimental setup (including flow sheet) and procedure should be clearly described (such that the experiment could be repeated by the reader). The applied key equations should be introduced and shortly explained.
- **Results and Discussion:** Experimental results are clearly presented graphically or in tables with error bars and R^2-values when appropriate. Key findings are presented and discussed related to the experimental objectives and background theory. The main uncertainties and sources of error are discussed. The validity of applied assumptions is evaluated. Important graphs to be included are:

$$X_{CO_2} \text{ as a function of } p_{CO_2}$$
$$\ln(-r_{CO_2}) \text{ as functions of } \ln(p_{CO_2})$$
$$X_{CO_2} \text{ as a function of } T$$
$$\ln(k) \text{ as functions of } 1/T$$

- **References:** Any applied references should be cited properly.
- **Appendix:** May include any material too detailed for the main report, such as the lab journal, experimental raw data, calibration curves, example calculations or scripts.

Note that a separate abstract, theory or conclusions section is not required in this course. A first report may be delivered (optional) to the supervisor <u>maximum 1 week</u> after the lab day for feedback. The final report should be delivered to the supervisor <u>maximum 1 week</u> after receiving feedback on the first report. Please deliver a reasonably complete first report, to get the most out of this opportunity.

A.3. Micro-GC Method

The micro-GC method parameters applied in this experiment is listed in **Table A.3.1**.

Table A.3.1: *Micro-GC method parameters.*

Sampling Time [s]:	30
Inlet Heating [°C]:	100
Run Time [s]:	350
Injector Heating [°C]:	110
Column Heating [°C]:	100
Injection Time [ms]:	80
Backflush Time [s]:	13
Column Pressure [Psi]:	10

A.4. MFC Calibration Data

The N_2 MFC calibration data is reported in **Table A.4.1**.

Table A.4.1: *Calibration data for N_2 MFC.*

MFC Setpoint [%]	Flow [mL/min] (a)
10.0	22.8
20.0	45.4
30.0	67.3
40.0	89.1
50.0	113
60.0	133
70.0	154
80.0	176
90.0	199

(a) Measured with Agilent ADM Flow Meter
at standard conditions (1 atm and 0 °C).

The He MFC calibration data is reported in **Table A.4.2**.

Table A.4.2: *Calibration data for He MFC.*

MFC Setpoint [%]	Flow [mL/min] (a)
10.0	21.7
20.0	43.0
30.0	64.1
40.0	84.9
50.0	105
60.0	127
70.0	148
80.0	169
90.0	191

(a) Measured with Agilent ADM Flow Meter
at standard conditions (1 atm and 0 °C).

The CO_2 MFC calibration data is reported in **Table A.4.3**.

Table A.4.3: *Calibration data for CO_2 MFC.*

MFC Setpoint [%]	Flow [mL/min] (a)
10.0	0.57
20.0	3.25
30.0	4.86
40.0	7.63
50.0	10.1
60.0	12.4
70.0	14.8
80.0	17.0
90.0	19.1

(a) Measured with Agilent ADM Flow Meter
at standard conditions (1 atm and 0 °C).

The H$_2$ MFC calibration data is reported in **Table A.4.4**.

Table A.4.4: *Calibration data for H$_2$ MFC.*

MFC Setpoint [%]	Flow [mL/min] (a)
10.0	22.7
20.0	47.4
30.0	74.5
40.0	102
50.0	129
60.0	156
70.0	185
80.0	213
90.0	240

(a) Measured with bubble flow meter and converted to standard conditions (1 atm and 0 °C).

A.5. Overview of Applied Conditions

Table A.5.1: *Overview of the applied calibration and experimental conditions.*

		MFC Setpoint [%] (a)				Volume Flow [mL/min] (b)				Volume Fraction [vol%] (b)				Total Flow [mL/min] (b)	Temperature			Dwell Time [min] (c)	Reactor Bypass
		CO_2	H_2	N_2	He	CO_2	H_2	N_2	He	CO_2	H_2	N_2	He		Start [°C]	End [°C]	Ramp [°C/min]		
GC Calibration	Level 1									5	60	15	20	200	RT	RT	0	NA	Yes
	Level 2									7.5	60	15	17.5	200	RT	RT	0	NA	Yes
	Level 3									10	60	15	15	200	RT	RT	0	NA	Yes
Temperature Programmed Experiment	Reduction	0			0	0			0	0	50	50	0	200	RT	350	10	0	No
	Step 1									5	60	15	20	200	350	350	0	45	No
	Step 2									7.5	60	15	17.5	200	350	350	0	45	No
	Step 3									10	60	15	15	200	350	350	0	45	No
	Step 4									10	60	15	15	200	350	360	10	45	No
	Step 5									10	60	15	15	200	360	370	10	45	No
	Cool-down	0	0		0	0	0		0	0	0	100	0	100	370	RT	10	NA	No

(a) Determined from MFC calibration curves based on the provided calibration data.
(b) At standard conditions (1 atm and 0 °C).
(c) Dwell time at temperature program step end temperature.

RT = Room temperature
NA = Not applicable