

Work Plan RE6 - Heterogeneous Catalyzed Reaction

Methanation of CO₂ over a Ru/Al₂O₃ Catalyst

1 Introduction

In this experiment, the CO₂ methanation reaction will be investigated at various reaction conditions over a Ru-based catalyst. The methanation of CO₂ using green H₂ is of great interest, since it can reduce carbon emissions while producing methane that can be stored long-term or used as fuel.^[1] The experiment will be conducted in a fixed bed quartz reactor in H₂-rich surroundings at atmospheric pressure and temperatures of 350-370 °C. Micro gas chromatography (micro-GC) will be used to analyze the effluent gas. The reaction order for CO₂ will be determined by varying the partial pressure of CO₂ and assuming a power-law rate model, and the activation energy will be determined by altering the reactor temperature and using Arrhenius' equation.

2 Experimental

2.1 Preparation of the Reactor

1. Load the reactor with the Ru/Al₂O₃ catalyst (300 mg) containing 2 wt% Ru on a γ -Al₂O₃ support
2. Dilute the catalyst bed with inert SiC (700 mg) to ensure isothermal conditions
3. Place a plug of quartz wool above and below the catalyst bed
4. Close the reactor and place it inside the oven, then connect the gas feed and outlet lines
5. Place the thermocouple inside the thermocouple holder in the reactor center to ensure proper monitoring of the reaction temperature
6. Perform a two step leak test by first using N₂ with a leak detection spray and then H₂ with a flammable gas detector
7. Run a N₂ gas flow (minimum 100 mL/min) through the reactor and then through the reactor bypass, both for 15 minutes each, to remove air from the system
8. Isolate the oven and switch on the condenser cooling water

2.2 Calibration of the Micro-GC

1. Set the three-way valves to direct the gas flow through the reactor bypass
2. Introduce the four gases one by one while analyzing the flow with the micro-GC to identify the peak position of the different components in the chromatogram and thereby determine the retention time for each component

2.3 Catalyst Pretreatment

1. To reduce Ru, run a gas flow of 50 vol% H₂ in N₂ over the catalyst bed while heating it from room temperature to 350 °C at a rate of 10 °C per minute

2.4 Kinetic Experiment

The kinetic experiment is divided into two parts:

1. Keep the reactor temperature constant at 350 °C while varying the gas composition every 45 minutes for a total of three different gas compositions. This part of the experiment is done to determine the CO₂ reaction order.
2. Keep the last gas composition from part one constant, while increasing the reactor temperature from 350 °C to 370 °C at a rate of 10 °C per minute. This part of the experiment is done to determine the activation energy of the reaction.

2.5 System Shutdown

1. Let the system cool down to room temperature at a rate of 10 °C per minute while purging with N₂ (100 mL/min)
2. Turn the cooling water off when the system reaches room temperature

3 Risk Assessments

Lab coat and goggles are to be worn at all times when in the laboratory. Gloves should be worn only when necessary, e.g. when loading the reactor. In addition, a dust mask is required when insulating the reactor.

The risks associated with this experiment mainly include high temperatures in the heating furnace and gas leakage from the system. The experiment is carried out with high temperatures in the heating furnace, which should not be touched to avoid burns. The gases used in the experiment are non-toxic, and gas detectors will alert in case of leakage of flammable gases. In addition, a leak test is performed before the experiment to minimize the risk of leakage.^[2]

References

- [1] Michael Specht, Jochen Brellochs, Volkmar Frick, Bernd Stuermer, Ulrich Zuberbuehler, Michael Sterner, and Gregor Waldstein. Storage of renewable energy in the natural gas grid. *Erdöl Erdgas Kohle*, 126, 2010.
- [2] Gunn Torill Wikdahl. Felleslab 2019 - re6 - kinetics for a heterogenous catalyzed reaction, 2015. hentet 21.09.2021.
- [3] Ask Lysne. Methanation of CO₂ over a Ru/Al₂O₃ catalyst. URL https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/RE6_heterogeneous_catalysed_reaction.pdf.

A Calculations

A.1 Molar Flow Rates

The MFC input signals in table A.1 are found using the following equations:

$$\begin{aligned} S_{\text{CO}_2} &= 4.28 \cdot F_{\text{CO}_2} + 7.34 \\ S_{\text{H}_2} &= 0.366 \cdot F_{\text{H}_2} + 2.49 \\ S_{\text{N}_2} &= 0.457 \cdot F_{\text{N}_2} - 0.709 \\ S_{\text{He}} &= 0.474 \cdot F_{\text{He}} - 0.254 \end{aligned} \quad (\text{A.1})$$

Here, F is the flow rate and S is the MFC input signal. These equations were found from linear regression of the MFC input signals as functions of the flow rates, which were plotted using the given calibration data.^[3]

Table A.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	50.14	46.36	12.99	18.72	10	120	30	40	5	60	15	20	200	RT	RT	0	NA	Yes
	Level 2	71.54	46.36	12.99	16.34	15	120	30	35	7.5	60	15	17.5	200	RT	RT	0	NA	Yes
	Level 3	92.94	46.36	12.99	13.97	20	120	30	30	10	60	15	15	200	RT	RT	0	NA	Yes
Temperature Programmed Experiment	Reduction	0	39.05	44.95	0	0	100	100	0	0	50	50	0	200	RT	350	10	0	No
	Step 1	50.14	46.36	12.99	18.72	10	120	30	40	5	60	15	20	200	350	350	0	45	No
	Step 2	71.54	46.36	12.99	16.34	15	120	30	35	7.5	60	15	17.5	200	350	350	0	45	No
	Step 3	92.94	46.36	12.99	13.97	20	120	30	30	10	60	15	15	200	350	350	0	45	No
	Step 4	92.94	46.36	12.99	13.97	20	120	30	30	10	60	15	15	200	350	360	10	45	No
	Step 5	92.94	46.36	12.99	13.97	20	120	30	30	10	60	15	15	200	360	370	10	45	No
	Cool-down	0	0	44.95	0	0	0	100	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

A.2 Gas Chromatography

To find the CO₂ conversion, data from gas chromatography will be used. But first, the GC apparatus must be calibrated. This is done by analyzing gas mixtures with known compositions, and from this determining the response factor of a component along with its retention time. The response factor RF_i for a compound i can be expressed as

$$RF_i = \frac{A_i}{y_i}, \quad (\text{A.2})$$

where A_i is the peak integration area and y_i is the molar fraction. In this experiment, the internal standard method will be used to calibrate the GC apparatus, with the inert gas N₂ functioning as the internal standard. The response factor for the internal standard RF_{IS} is then used to define a relative response factor RRF_i :

$$RRF_i = \frac{RF_i}{RF_{IS}}. \quad (\text{A.3})$$

Combining equation (A.2) and (A.3) and introducing molar flow F gives:

$$RRF_i = \frac{A_i}{y_i} \frac{y_{IS}}{A_{IS}} \frac{F_{tot}}{F_{tot}} = \frac{A_i}{A_{IS}} \frac{F_{IS}}{F_i}. \quad (\text{A.4})$$

The molar flow rate F of component i is then found by solving for F_i :

$$F_i = \frac{A_i}{A_{IS}} \frac{F_{IS}}{RRF_i}. \quad (\text{A.5})$$

The conversion of CO_2 , X_{CO_2} , can be calculated using equation (A.6):

$$X_{\text{CO}_2} = \frac{F_{\text{CO}_2}^0 - F_{\text{CO}_2}}{F_{\text{CO}_2}^0}. \quad (\text{A.6})$$

A.3 Reaction Rate

The rate of CO_2 consumption, $-r_{\text{CO}_2}$, is given by

$$-r_{\text{CO}_2} = kp_{\text{CO}_2}^a p_{\text{H}_2}^b, \quad (\text{A.7})$$

where 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. The reaction rate can be considered independent of the partial pressure of H_2 in a H_2 -rich atmosphere ($b = 0$), and thus equation (A.7) becomes

$$-r_{\text{CO}_2} = kp_{\text{CO}_2}^a. \quad (\text{A.8})$$

The reaction rate is related to the conversion level by

$$-r_{\text{CO}_2} = \frac{F_{\text{CO}_2}^0 X_{\text{CO}_2}}{\Delta W}, \quad (\text{A.9})$$

where $F_{\text{CO}_2}^0$ is the molar flow rate of CO_2 at the reactor inlet, X_{CO_2} is the CO_2 conversion and ΔW is the mass of the applied catalyst.

A.4 Reaction Order

Linearization of equation (A.8) gives

$$\ln(-r_{\text{CO}_2}) = \ln(k) + a \cdot \ln(p_{\text{CO}_2}). \quad (\text{A.10})$$

Plotting $\ln(-r_{\text{CO}_2})$ as a function of $\ln(p_{\text{CO}_2})$, and performing linear regression analysis, gives the reaction order, a , as the slope of the straight line function, and the rate constant, k , as the intersection between the straight line and the y-axis.

A.5 Activation Energy

The activation energy E_A can be found by measuring $-r_{CO_2}$ at different temperatures and finding the rate constant k from equation (A.7). Arrhenius' equation given in (A.11)

$$k = AE^{-\frac{E_A}{RT}} \quad (\text{A.11})$$

can be linearized to get:

$$\ln k = \ln A - \frac{E_A}{RT}. \quad (\text{A.12})$$

When plotting $\ln k$ against $\frac{1}{T}$, $-\frac{E_A}{R}$ is the slope of the curve and $\ln A$ is the intercept value.