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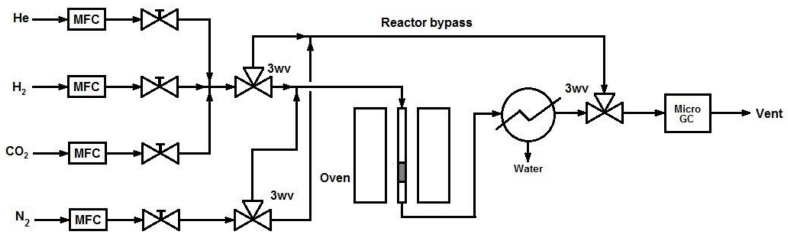
RE6 - Heterogeneous Catalyzed Reaction Methanation of CO_2 over a Ru/Al_2O_3 catalyst

1 Introduction

In this experiment a CO_2 methanation reaction is being carried out at different reaction conditions over a Ru/Al_2O_3 catalyst. The reactor used is a fixed bed quartz reactor in H_2-rich atmosphere. After going through the reactor, the gases will be analysed using micro gas chromatography (Micro GC). The goal of the experiment is determining the species' reaction orders and the activation energy of the reaction. This will be done by varying the partial pressure of CO_2 and the temperature, respectively.

2 Experimental procedure



Figur 2.1: Simplified flow chart of the experiment and the testing apparatus used. Mass-flow controllers (MFC), three-way valves (3wv) and gas chromatograph (GC).

2.1 Preparation of Reactor

In this experiment a catalyst testing apparatus will be utilized. The catalyst is Ru/Al_2O_3 (300 mg), containing 2wt% Ru on a γ-Al_2O_3 support.

- Prepare the reactor, by placing a small plug of quartz wool in the bottom of the reactor.
- Dilute the catalyst with 700mg SiC. Then load into the reactor.
- Place a plug of quartz wool above the catalyst bed.
- Close up and place the reactor in the oven, before connecting the gas feed and outlet lines.
- Place the thermocouple inside its holder, located in the reactor center. This will accurately monitor the reaction temperature.
- Test the reactor for leakage, by first flowing N_2 through the reactor while using detection spray. Then using H_2 and a flammable gas detector.
- Clear the system by N_2 (100 ml/min) first through the reactor, then the reactor bypass, both for 15 min
- Isolate the oven and turn on the cooling water

The following steps are done to calibrate the micro-GC:

- Start the three way flow through the reactor bypass

- Introduce one gas at the time, to identify the peak position if each component in the micro GC. Define the retention time, by locating the time of peak maximum. The values are given in figure A.1.

The relative response factor of CO_2 with respect to the internal standard N_2 can be calculated.

2.2 Catalyst Pretreatment

To activate the catalyst Ru needs to be reduced to its metallic state.

- Reduce Ru by inducing a flow of 50% H_2 in N_2, while gradually increasing the temperature from 25 °C to 350 °C at 10 °C per minute.

2.3 Kinetic Experiment

The experiment is divided into 2 parts. Part 1 consists of steps 1-3, where the temperature is constant and the composition of the gases vary. The data from part 1 is used to determine the reaction order of CO_2. Part 2 consists of steps 3-5, where the composition is kept constant, and the temperature varies. The data from part 2 is used to determine the activation energy of the reaction. The Micro GC continuously analyses the composition of the product gas. For stepse 1-3, the gases are analysed for 45 minutes, before changing the composition. For steps 3-5 the heating rate is set to 10 °C/min.

2.4 Shut Down

- Let the system cool down to 25°C, while purging with N_2
- Close He, H_2, and CO_2 gas feeds
- Turn the cooling water off when the system reaches. [1]

3 Risk analysis

Lab coat and goggles will be worn at all times during the experiment. Gloves should only be worn when necessary, such as when one is loading the reactor. While insulating the reactor, a dust mask is required, because insulation fibers create a dust that can be irritating if inhaled.

There are few risks related to this experiment. Spillage on user and on surfaces are likely because the catalyst powder is light weight and sensitive to static and air fluctuations. However the powder is not toxic and will in that case just cause some irritation for the skin and eyes. The gases being used in the experiment are non-toxic, and a leak test is done prior to the experiment to minimize the risk of leakage. The experiment is performed with high temperatures, and the oven should therefore not be touched to avoid burns. Waste is to be thrown in their respectable waste containers. [2]

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Referanser

[1] Ask Lysne. Re6 - kinetics: Heterogeneous catalyzed reaction methanation of CO_2 over a Ru/Al_2O_3 catalyst. URL `https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/RE6_heterogeneous_catalysed_reaction.pdf`.

[2] Gunn Torill Wikdahl. Felleslab 2019 - re6 - kinetics for a heterogenous catalyzed reaction, 2015. Hentet 15.09.21 .

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A Calculations

A.1 Rate of consumption

The rate of CO_2 consumption, $-r_{CO_2}$, is given by:

$$\begin{aligned} -r_{CO_2} &= k p_{CO_2}^a p_{H_2}^b \\ -r_{CO_2} &= k p_{CO_2}^a, \end{aligned} \tag{A.1}$$

where k is the rate constant, p_{CO_2} and p_{H_2} are the partial pressures for their respective reactants, and a and b are the reaction orders for CO_2 and H_2 respectively. The formula can simplified as shown in equation A.1, because in a H_2-rich atmosphere, the reaction rate is considered independent of H_2 partial pressure (b=0).

Another way to write the consumption of CO2, at low conversion levels, is:

$$-r_{CO_2} = \frac{F_{CO_2,0} X_{CO_2}}{\Delta W}. \tag{A.2}$$

Here $F_{CO_2,0}$ is the feed rate of CO_2, X_{CO_2} is the conversion rate, and ΔW is the catalyst sample mass.

A.2 Reaction order

To find the reaction rate and reaction order, equation A.1 is rewritten as:

$$ln(-r_{CO_2}) = lnk + \alpha \cdot ln(p_{CO_2}) \tag{A.3}$$

Here k and α is the rate constant and the reaction order respectively. These can be found by plotting $\ln(-r_{CO_2})$ with respect to $\ln(p_{CO2})$. The reaction order is then given by the slope value, and the rate constant is the intercept value.

A.3 Activation energy

The activation enery, E_A can be found by rewriting the Arrhenius equation:

$$\begin{aligned} k &= A e^{\frac{-E_A}{RT}} \\ lnk &= lnA - \frac{E_A}{RT} \end{aligned} \tag{A.4}$$

Here A is the constant pre-exponential factor, R is the universal gas constant, and T is the temperature of the reactor. By plotting lnk as a function of $\frac{1}{T}$, $\frac{E_A}{R}$ and lnA can be found as the slope value and the intercept value, respectively.

A.4 CO_2 conversion

In this experiment gas chromatography (GC) is going to be used to to find the CO_2 conversion. The response factor, RF_i, for a component i is defined by:

$$RF_i = \frac{A_i}{x_i}, \tag{A.5}$$

where A_i is the peak integration and x_i is the molar fraction of i.

Before analysing, the GC apparatus needs to be calibrated using the internal standard method, with N_2 as the internal standard. Then the amounts of all other components are determined relative to this standard. The relative response factor, RRF_i is given by:

$$\begin{aligned} RRF_i &= \frac{RF_i}{RF_{IS}} \\ &= \frac{A_i}{x_i}\frac{x_{IS}}{A_{IS}}, \end{aligned} \tag{A.6}$$

where RF_{IS}, A_{IS}, and a_{IS} are the response factor, the peak area, and the molar fraction for the internal standard, respectively.

By rewriting equation A.6, the molar flow rates can be calculated:[1]

$$F_i = \frac{A_i}{A_{IS}}\frac{F_{IS}}{RRF_i} \tag{A.7}$$

Then the CO_2 conversion can be calculated:

$$X_{\mathrm{CO_2}} = \frac{F_{\mathrm{CO_2},0} - F_{\mathrm{CO_2}}}{F_{\mathrm{CO_2},0}} \tag{A.8}$$

A.5 Flow rates and MFC input signal

The flow rates and MFC input signals in table A.1 are found by using A.9-A.12.

$$S_{\mathrm{CO_2}} = 4.280 \cdot F_{\mathrm{CO_2}} + 7.336 \tag{A.9}$$

$$S_{\mathrm{H_2}} = 0.366 \cdot F_{\mathrm{H_2}} + 2.495 \tag{A.10}$$

$$S_{\mathrm{N_2}} = 0.457 \cdot F_{\mathrm{He}} - 0.709 \tag{A.11}$$

$$S_{\mathrm{He}} = 0.474 \cdot F_{\mathrm{He}} - 0.254 \tag{A.12}$$

These were found by using the given calibration data[1] for each component, and plotting the MFC setpoints, S_i, as a function of the flow rates, F_i, and using linear regression.

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	50,14	46,42	13,00	18,71	10	120	30	40	5	60	15	20	200	RT	RT	0	NA	Yes
	Level 2	71,54	46,42	13,00	16,34	15	120	30	35	7.5	60	15	17.5	200	RT	RT	0	NA	Yes
	Level 3	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	RT	RT	0	NA	Yes
Temperature Programmed Experiment	Reduction	0	39,10	44,99	0	0	100	100	0	0	50	50	0	200	RT	350	10	0	No
	Step 1	50,14	46,42	13,00	18,71	10	120	30	40	5	60	15	20	200	350	350	0	45	No
	Step 2	71,54	46,42	13,00	16,34	15	120	30	35	7.5	60	15	17.5	200	350	350	0	45	No
	Step 3	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	350	350	0	45	No
	Step 4	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	350	360	10	45	No
	Step 5	92,94	46,42	13,00	13,97	20	120	30	30	10	60	15	15	200	360	370	10	45	No
	Cool-down	0	0	44,99	0	0	0	100	0	0	0	100	0	100	370	RT	10	NA	No

Figur A.1: Completed overview of applied conditions with the required MFC setpoints and volumetric feed flows