

Experimental approach for identifying hotspots in lab-scale fixed-bed reactors exemplified by the Sabatier reaction

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Abstract Isothermal conditions are a prerequisite for the accurate determination of kinetics in heterogeneous catalysis. In this work, an integral fixed-bed lab reactor with 5 mm inner diameter placed inside an aluminum heating block is used. Temperature profiles were recorded with a single but axially movable thermocouple in a fixed bed of a highly loaded supported Ni catalyst (15.4 wt% Ni on γ -Al₂O₃) for the Sabatier reaction, i.e., the methanation of CO₂, under elevated pressures and without carrier gas dilution. The corresponding conversions of CO₂ were determined at the reactor outlet. Depending on the reaction conditions, temperature profiles can show significant deviations from isothermal conditions and even a light-off phenomenon with fluctuating conversions seems to occur. Based on our results, an experimental approach based on the use of one single thermocouple in the fixed bed is recommended which allows to exclude the occurrence of hotspots with a high degree of certainty.

Keywords Sabatier reaction · Kinetic measurements · Isothermal fixed bed · Hotspots · Light-off phenomenon

Introduction

The kinetics of chemical reactions are indispensable for the basic engineering of chemical reactors in the chemical industry [1]. For the design and the operation of reactors, the dependence of the reaction rate on the operation conditions, i.e.,

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temperature, pressure and concentrations, needs to be known. Thus, kinetic measurements have to be conducted and parameter estimation as well as model discrimination performed [2]. In order to get reliable and accurate rate equations, the kinetic data must be determined without heat and mass transport limitations [3]. Thus, the choice of the laboratory reactor for kinetic measurements is essential [4]. In many cases, a fixed-bed tubular reactor is used for kinetic investigations in the lab [3].

Kinetic measurements in the fixed-bed tubular reactor can be performed by the integral or differential approach. In the differential approach, the conversion is kept low so that the concentrations in the fixed bed can be assumed to stay nearly constant between inlet and outlet of the reactor. Hereby, it is possible to calculate the reaction rates directly from the measured conversions [2]. For justifying the assumption of constant concentrations in the reactor, a conversion $< 5\%$ is generally required. However, it is a controversial discussion up to which conversion this assumption is really fulfilled [4]. Due to the low conversion, the heat of reaction is small, and an isothermal conditions can be more easily realized. However, the small conversions are problematic with regard to product analytics and reaching an acceptable accuracy [5, 6]. Hence, fixed-bed tubular reactors are often operated at high conversions during kinetic investigations (integral approach) [5]. Since the concentrations are changing throughout the fixed bed, the reaction rates cannot be determined directly from the conversions any more. Thus, either the measured integral data have to be differentiated or the mass balance of the reactor has to be integrated to get the reaction rates. The advantages of the integral versus the differential operation of the fixed-bed reactor are the simpler and more precise analytics [4, 5]. Different conversions are achieved by variation of the volumetric flow rates, which leads to different product compositions in the fixed bed [7]. The main disadvantage of the integral operation of the fixed-bed reactor is that for highly exothermic reactions generating large amounts of heat, it is hardly possible to achieve isothermal conditions [5–8]. Especially for catalyzed reactions in the gas phase, the formation of temperature gradients in the fixed bed is critical, since the thermal conductivity and the heat capacity of the gas phase are smaller than in the liquid phase [3]. Also, the thermal conductivity of the fixed bed is small, since the porous catalyst particles have a lower thermal conductivity than the bulk material [5, 9], and the heat transport between the catalyst particles takes place mainly via the gas phase and the solid/gas heat transfer [3].

Isothermal conditions for the measurement of kinetic data are extremely important, since the reaction rate is significantly influenced by non-isothermal conditions due to the exponential temperature dependence [5]. Hence, there are different possibilities to avoid the formation of temperature gradients in the reactor. One possibility is the dilution of the catalyst with inert material [3, 10]. Anderson and Pratt point out that a strong dilution of the catalyst in the fixed bed with inert material creates new problems (bypass effects) [5]. Van den Bleek et al. propose a criterion for the estimation of the experimental error which is created by dilution [11]. In the meantime, a newer criterion exists which is supported by experimental and theoretical investigations [10]. A further possibility is to dilute the feed with inert gas [12]. However, a high dilution with inert gas creates the same problems as

the differential method, e.g., problems with product analytics and small partial pressures of the products in the reactor. Additionally, the range of validity of such kinetics is limited and often not relevant for undiluted technical conditions.

Besides diluting the catalyst and the feed, the reactor diameter is an important parameter for preventing temperature gradients in the reactor. The radial heat conduction to the reactor wall through multiple solid/gas heat transfer steps is the most important parameter for minimizing the temperature gradients in the reactor [3]. A smaller reactor diameter enables better heat transport and is, hence, of utmost importance [3, 5]. However, the reactor diameter can only be decreased to a certain extent without creating new perturbing effects. It is generally assumed that bypassing of the fluid along the reactor wall can be neglected if the reactor diameter is 10 times larger than the particle size [3]. Hence, all measures for avoiding temperature gradients have only limited applicability.

The temperature should be measured directly in the fixed bed so that the conversion can be related to the precise reaction temperature. The temperature is usually determined with a thermocouple, which is introduced at the end of the fixed bed against the flow direction [3, 5, 8]. However, introducing the thermocouple into the fixed bed leads to a perturbation of the fluid dynamics, e.g., bypassing of the fluid along the wall of the thermocouple [7]. These fluid dynamic effects become more important the smaller the difference is between the inner diameter of the reactor and the diameter of the thermocouple. This difference is especially small for laboratory reactors since these often have an inner diameter of 4–6 mm [3], and thermocouples usually have a diameter of 1/16" (about 1.6 mm).

In this work, the isothermality of a fixed-bed tubular reactor is investigated during the methanation of CO₂. In recent years, CO₂ methanation has received great attention because methane can be used as chemical storage for excess electrical energy. In the power to gas (PtG) process, excess electrical energy is used to produce H₂ via H₂O electrolysis [13]. There are different CO₂ sources available, e.g., coal fired power plants, biogas plants or cement industries. In a new approach, a mixture of H₂, CO and CO₂ is produced in a single step by alkaline H₂O electrolysis on graphite electrodes performing the hydrogen evolution reaction on the cathode side and the carbon oxidation reaction towards CO/CO₂ on the anode side [14]. It is possible to replace the graphite electrodes with a renewable carbon source.

The methanation of CO₂ is the so-called Sabatier reaction, which is highly exothermic:



Preliminary investigations of the methanation of CO₂ showed that the fixed bed is probably not isothermal. Also other work on the methanation of CO [15], CO₂ [16–18] and CO/CO₂ [19] reports about significant temperature gradients which suggests that during kinetic measurements of the CO₂ methanation isothermal conditions are difficult to achieve. Hence, the isothermality of the fixed bed was closely investigated in this work. For researchers working in catalysis laboratories, the results reported here can be helpful to ensure isothermal conditions also in other kinetic investigations by following a purely experimental approach.

Experimental section

The catalyst 15.4 Ma.-% Ni/ γ -Al₂O₃ was synthesized via deposition precipitation and analyzed via atomic emission spectroscopy with inductively coupled plasma (Varian, Vista-MPX). The catalyst was reduced in a quartz glass reactor at 600 °C (heating rate 3 °C min⁻¹) for 1 h with hydrogen ($\dot{V}_{\text{H}_2}/\dot{V}_{\text{N}_2} = 0.43$). The modified residence time τ_{mod} was calculated from the ratio of the catalyst mass and the total volumetric flow rate. The volumetric flow rates and the calculated parameters are given at standard conditions (STP). All gases were supplied by Westfalen AG [hydrogen (5.0), carbon dioxide (4.5), argon (4.6), nitrogen (5.0)]. The volumetric flow rates were controlled with mass flow controllers by Bronkhorst.

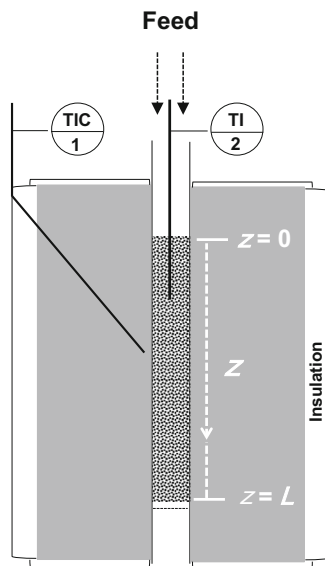
The tubular reactor made from stainless steel had an inner diameter of 5 mm and contained a glass frit. The glass frit was covered with glass wool (about 5 mm height). The pre-reduced catalyst was mixed in a snap cap vial with SiC as inert material with the same particle size (0.200–0.315 mm). To ensure a homogeneous mixtures the vial was carefully turned and rotated for 1 min. The mixture of the catalyst and SiC was filled into the reactor using a paper funnel in order to avoid the buildup of electrostatic charges and the subsequent separation of the catalyst and SiC in the reactor. The length of the fixed bed (L) changed between ≈ 5 and ≈ 10 cm depending on the catalyst mass and the dilution.

For heating the reactor, an aluminum block with two heating cartridges of 25 cm was used. The aluminum block consisted of two aluminum plates with cavities which fitted exactly to the corresponding reactor. The reactor was surrounded by these two aluminum plates which are pressed together by screw connection. A close fitting of the aluminum block is important to ensure a close contact between the reactor and the aluminum block. If the fitting is not close enough, the gas gap results in a low thermal conductivity.

The aluminum block was insulated by a heat-resistant glass fiber tape. The temperature of the aluminum block (T_1) was measured with a thermocouple (type K, outer diameter 1/16") close to the fixed bed (Fig. 1) and controlled through the heat output of the heating cartridge. The temperature profile in the fixed bed (T_2) was measured via a movable thermocouple. For this purpose, a hole with the diameter of the thermocouple was drilled into a 1/16"GC-graphite seal. The thermocouple could be moved during the reaction at atmospheric pressure without leakage. For measuring the fixed-bed temperature under pressure, the pressure had to be released before the thermocouple was moved to a new position.

The activity of SiC and the reactor steel were investigated in a blank test. No significant conversion could be found at $p_{\text{abs}} = 1.6$ MPa and $T = 400$ °C ($X_{\text{CO}_2} < 1\%$). Gas analysis was carried out using gas chromatography (GC, HP 6890) and an NDIR detector (ABB 3020, URAS26). The gas chromatograph was equipped with column switching, where the gas sample was led onto a Hayesep-Q column (separation of H₂O, CO₂ and C₂₊ hydrocarbons) and a molecular sieve column (separation of H₂, Ar, N₂, CO, CH₄). The components were detected with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The response factors of the components were determined by external calibration and allowed to

Fig. 1 Scheme of the reactor with thermocouples in the aluminum block (TIC_1) and in the fixed bed (TI_2)



calculate the molar amounts in the sample loop. The GC conversion of CO_2 was determined using a bypass experiment with an internal standard according to Eq. (2). In order to take the volume contraction into account, about 1.5 vol.% of argon was added as internal standard. Thus, the volume contraction is included through the ratio of the argon peak area of the bypass experiment $A(\text{Ar})_{\text{in}}$ and during the reaction $A(\text{Ar})_{\text{out}}$. The carbon balance was closed to $\pm 1\%$. The selectivity to CO was $< 5\%$, and only traces of ethane could be detected.

$$X(\text{CO}_2, \text{GC}) = \frac{n(\text{CO}_2)_{\text{in}} - n(\text{CO}_2)_{\text{out}} \cdot \left(\frac{A(\text{Ar})_{\text{in}}}{A(\text{Ar})_{\text{out}}} \right)}{n(\text{CO}_2)_{\text{in}}} \quad (2)$$

Since the internal standard could not be detected by NDIR, the IR conversion of CO_2 was calculated via using a balance approach of the molar amounts in the cuvette according to Eq. (3). The conversions determined by gas chromatography and NDIR were in perfect agreement.

$$X(\text{CO}_2, \text{IR}) = \frac{n(\text{CH}_4)_{\text{out}} + n(\text{CO})_{\text{out}}}{n(\text{CO}_2)_{\text{out}} + n(\text{CH}_4)_{\text{out}} + n(\text{CO})_{\text{out}}} \quad (3)$$

The equilibrium conversions were taken from Gao et al. [20]. Since they did not calculate the equilibrium conversion at 1.6 MPa, the equilibrium conversion is given at 1.013 and 3.040 MPa. In the relevant temperature range, the difference between the equilibrium conversions at 1 and 3 MPa is small.

Results

The conversion of CO_2 was measured at constant modified residence time and temperatures from 200 to 350 °C (Fig. 2). Each temperature was held for at least 30 min. During the first experiment (Run 1), there is an abrupt rise of the conversion from 25 to 91% between 280 and 290 °C. During the second and third experiment, the conversion jump can be observed at temperatures between 270 and 280 °C (Run 2) and between 280 and 290 °C (Run 3). The abrupt rise of the conversion indicates a light-off phenomenon. The light-off at lower temperature at the second run is an indication for the sensitivity of this phenomenon, for instance a slightly higher heating rate could cause the light-off at a lower temperature. The conversion of the second and the third run before the light-off is smaller than the conversion of the first run due to the deactivation of the catalyst.

The time-on-stream behavior of the first experiment (Run 1) is given in Fig. 3 (left). First, the temperatures from 200 to 350 °C are measured. Afterwards, the system is allowed to cool down to 270 °C. However, the conversion is fluctuating and stays at much higher values than in the heat-up cycle despite the same measured temperature of 270 °C (hysteresis). During the second experiment (Run 2), the measured temperature rise from 270 to 280 °C leads to a significant conversion jump and a fluctuating conversion, whereas a further temperature rise to 285 °C has no significant impact on the conversion any more (Fig. 3, right). This small dependence of the conversion on the reactor temperature after the abrupt conversion rise, the fluctuations and the hysteresis point to a large effect of the heat evolution in the fixed bed. However, the temperature of the fixed bed, which is measured in the middle of the fixed bed, does not confirm this assumption. Hence, it is assumed that a hotspot evolves in the first part of the fixed bed, which cannot be measured in the middle of the fixed bed.

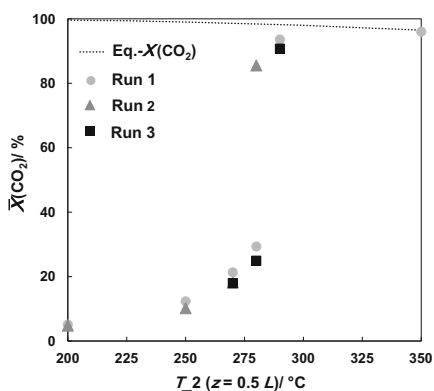


Fig. 2 Mean conversion of CO_2 in dependence of the temperature at $p_{\text{abs}} = 1.6$ MPa, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $\tau_{\text{mod}} = 50$ kg s m^{-3} ($\dot{V}_{\text{CO}_2+\text{H}_2} = 240$ ml min^{-1}), $m_{\text{cat.}} = 200$ mg, $m_{\text{SiC}}/m_{\text{cat.}} = 9$, T_2 at $z = 0.5$ L, i.e., the temperature was measured in the middle of the fixed bed. The equilibrium conversions (Eq.- $X(\text{CO}_2)$) at 3 MPa were taken from Gao et al. [20]

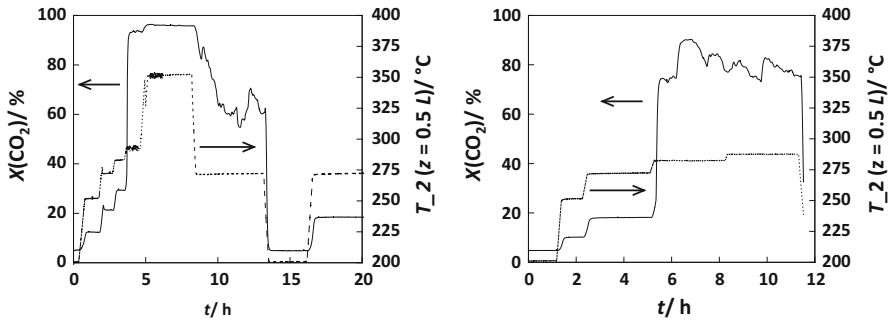


Fig. 3 Time-on-stream behavior of Run 1 (left) and Run 2 (right); $p_{\text{abs}} = 1.6 \text{ MPa}$, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $\tau_{\text{mod}} = 50 \text{ kg s m}^{-3}$ ($\dot{V}_{\text{CO}_2+\text{H}_2} = 240 \text{ ml min}^{-1}$), $m_{\text{cat.}} = 200 \text{ mg}$, dilution: $m_{\text{SiC}}/m_{\text{cat.}} = 9$, T_2 at $z = 0.5 \text{ L}$, i.e., the temperature was measured in the middle of the fixed bed

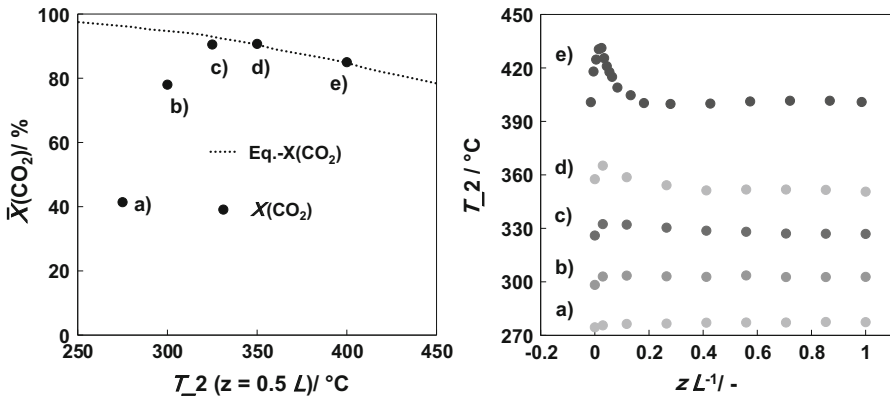


Fig. 4 Conversions (left) and the corresponding temperature profiles during the reaction (right); $p_{\text{abs}} = 0.1 \text{ MPa}$, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $\tau_{\text{mod}} = 230 \text{ kg s m}^{-3}$ ($\dot{V}_{\text{CO}_2+\text{H}_2} = 104 \text{ ml min}^{-1}$), $m_{\text{cat.}} = 400 \text{ mg}$, dilution: $m_{\text{SiC}}/m_{\text{cat.}} = 9$; **a** $\Delta T \approx 0 \text{ }^\circ\text{C}$, **b** $\Delta T \approx 1 \text{ }^\circ\text{C}$, **c** $\Delta T \approx 5 \text{ }^\circ\text{C}$, **d** $\Delta T \approx 15 \text{ }^\circ\text{C}$, **e** $\Delta T \approx 30 \text{ }^\circ\text{C}$; $\Delta T = T(\text{max}) - T(z \text{ L}^{-1} = 1)$, $L \approx 10.2 \text{ cm}$. The equilibrium conversions (Eq.- $X(\text{CO}_2)$) at 0.1 MPa were taken from Gao et al. [20]

This assumption is confirmed by measurements of the temperature profiles in the fixed bed by using a movable thermocouple. However, since the thermocouple could not be moved at higher pressures without creating leaks a pressure of 0.1 MPa was chosen instead of 1.6 MPa. At this pressure, the fixed bed was also at high conversions nearly isothermal (Fig. 4a, b). At a conversion close to the equilibrium conversion, there is a temperature gradient of about 5 °C at the reactor inlet (Fig. 4c). Once the equilibrium conversion is reached, the temperature gradient increases with a further temperature increase and moves further to the reactor inlet (Fig. 4d, e). The reason for this is the fact that there is a high reaction rate at these temperatures, and the reactants are completely converted already in the first part of the fixed bed until the equilibrium composition is reached.

For the verification of this statement, the volumetric flow rate of the reactants at 400 °C is increased. At all volumetric flow rates, the equilibrium conversion is

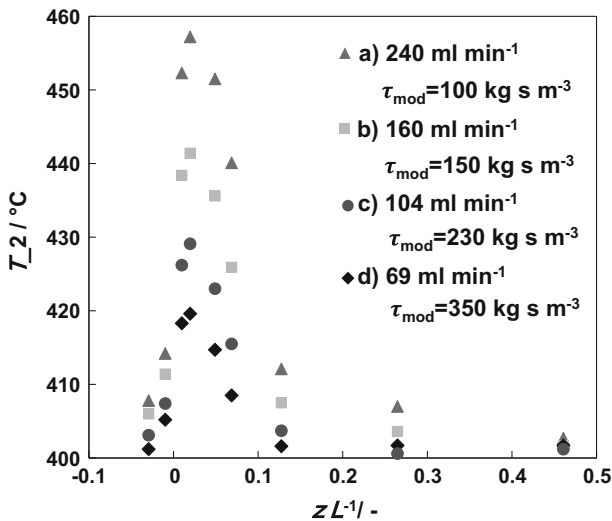


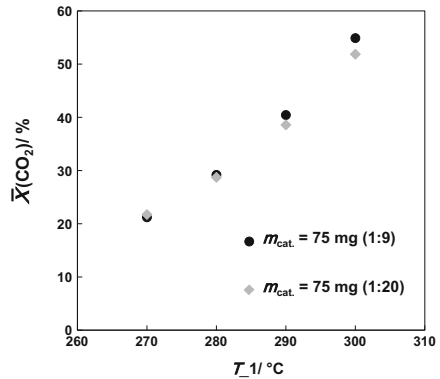
Fig. 5 Temperature profiles during the reaction at different volumetric flow rates $\dot{V}_{\text{CO}_2+\text{H}_2}$; $p_{\text{abs}} = 0.1$ MPa, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $m_{\text{cat.}} = 400$ mg, dilution: $m_{\text{SiC}}/m_{\text{cat.}} = 9$; $L \approx 10.2$ cm; $X(\text{CO}_2)$: equilibrium conversion (about 85%)

reached. Due to the higher heat evolution, the hotspot becomes more severe with increasing volumetric flow rate. The position of the temperature maximum is not changing (Fig. 5). Hence, the temperature profiles from Figs. 4 and 5 show the occurrence of hotspots which cannot be detected when measuring temperatures in the middle of the fixed bed ($z L^{-1} = 0.5$).

Even though the temperature profiles were measured at 0.1 MPa, they qualitatively explain the observations at 1.6 MPa: at the reactor inlet, the reactant concentration and hence the reaction rate are maximal. Thus, the first part of the fixed bed is most critical for the formation of hotspots. With increasing pressure, the reaction rate is increasing due to the higher reactant concentration whereby more heat is released. Due to the higher pressure, hotspots should be possible also at temperatures at which the equilibrium conversion is not reached, which cannot be detected in the middle of the fixed bed.

In the literature, it is suggested to check for isothermality by measuring the conversion at the same catalyst mass and the same volumetric flow rate, but at different dilutions [3, 5]. If the fixed bed is not isothermal, the conversion decreases with increasing dilution, since the local fixed-bed temperatures decrease due to the higher dilution. The fixed bed can be assumed to be isothermal if the conversion is independent of the dilution. Therefore, the dilution was increased from 1:9 to 1:20, and the conversions were compared for both measurements (Fig. 6). In order to measure at a dilution of 1:20, the catalyst mass was decreased to 75 mg for both measurements. If the heating block temperature T_1 is chosen as a reference point, it is possible to recognize different temperatures of the fixed bed by differences in the conversion, because at the same catalyst mass, the same volumetric flow rate

Fig. 6 Conversion in dependence of the temperature of the heating block at $p_{\text{abs}} = 1.6 \text{ MPa}$, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $\tau_{\text{mod}} = 50 \text{ kg s m}^{-3}$, $(\dot{V}_{\text{CO}_2+\text{H}_2} = 90 \text{ ml min}^{-1})$, $m_{\text{cat.}} = 75 \text{ mg}$, $m_{\text{SiC}}/m_{\text{cat.}} = 9$ and 20



and the same heating block temperature, the deviation of the conversion should mainly be caused by different temperature profiles in the fixed bed.

At low conversions, the measurements coincide (Fig. 6). With increasing conversion, the conversion at the higher dilution is slightly lower. The relative deviation of the conversions at 300 °C is 5 rel.-%. This indicates that the heat of reaction leads even at such high dilution ratios to higher local temperatures of the fixed bed at a lower dilution. Due to the higher heat evolution, this effect should become more significant with increasing conversion, which is indeed the case. However, the higher dilution also leads to a bypassing of the fluid. This has a bigger impact with higher conversions. However, according to the work of Berger et al. [10], the decrease of the conversion due to bypassing effects at 300 °C does not exceed 1.5 rel.-%.

These measurements indicate that heat effects must have an influence even at high catalyst dilution ratios of about 1:9. Since the previous results showed that a hotspot cannot be recognized by measuring the temperature in the middle of the fixed bed, the temperatures for the experiments with 75 mg catalyst and 1.6 MPa are in the following measured in the first quarter of the fixed bed. The reactor temperature is controlled via a thermocouple in the heating block close to the fixed bed (Fig. 1). Under flowing inert gas, the fixed bed is isothermal, and the temperature (T_2) is across the whole bed about 2 °C higher than the chosen temperature of the heating block (T_1). Thus, a deviation from this temperature difference hints at a significant heat evolution in the fixed bed. At 300 °C heating block temperature, the temperature in the fixed bed is 8.5 °C higher for $m_{\text{SiC}}/m_{\text{cat.}} = 9$ and 6 °C higher for $m_{\text{SiC}}/m_{\text{cat.}} = 20$. If the conversion is not referred to the heating block temperature, but to the temperature in the first quarter of the fixed bed, the conversion curves coincide (Fig. 7, left). Thus, measuring the temperature in the first quarter of the fixed bed seems to take account of the deviation from isothermal behavior in an acceptable way. To verify this assumption, the temperature of the fixed bed was measured at 1.6 MPa at different positions. Since the thermocouple cannot be moved under pressure, these measurements are time-consuming, which is why only three positions were measured. Fig. 7 right shows the deviation of the fixed-bed temperature from the heating block temperature at a heating block

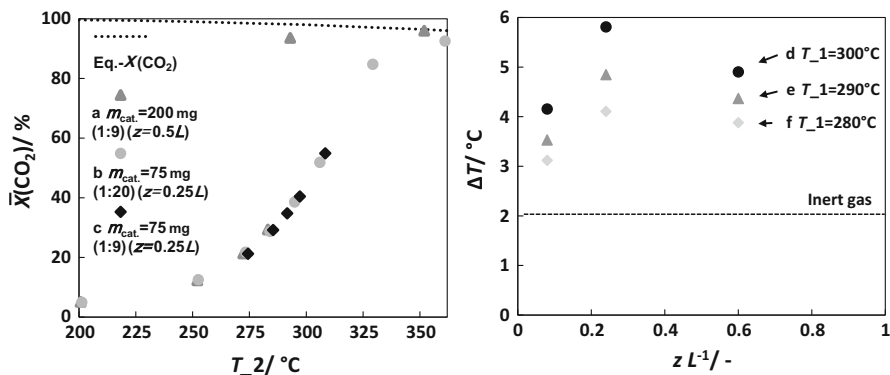


Fig. 7 Left: conversion in dependence of the temperature in the fixed bed at $p_{\text{abs}} = 1.6$ MPa, $\dot{n}_{\text{H}_2}/\dot{n}_{\text{CO}_2} = 4$, $\tau_{\text{mod}} = 50$ kg s m^{-3} for **a** $m_{\text{cat}} = 200$ mg, $m_{\text{SiC}}/m_{\text{cat}} = 9$, $\mathcal{V}_{\text{CO}_2+\text{H}_2} = 240$ ml min^{-1} , T_2 at $z = 0.5$ L, **b** $m_{\text{cat}} = 75$ mg, $m_{\text{SiC}}/m_{\text{cat}} = 20$, $\mathcal{V}_{\text{CO}_2+\text{H}_2} = 90$ ml min^{-1} , T_2 at $z = 0.25$ L, and **c** $m_{\text{cat}} = 75$ mg, $m_{\text{SiC}}/m_{\text{cat}} = 9$, $\mathcal{V}_{\text{CO}_2+\text{H}_2} = 90$ ml min^{-1} , T_2 at $z = 0.25$ L; right: deviation of the fixed-bed temperature from the heating block temperature $\Delta T = T_2 - T_1$, $m_{\text{cat}} = 75$ mg, $m_{\text{SiC}}/m_{\text{cat}} = 20$, $L \approx 5$ cm, **d** $T_1 = 300$ °C, $X(\text{CO}_2) \approx 48\%$, **e** $T_1 = 290$ °C, $X(\text{CO}_2) \approx 36\%$, **f** $T_1 = 280$ °C, $X(\text{CO}_2) \approx 27\%$. The equilibrium conversions (Eq.- $X(\text{CO}_2)$) at 3.0 MPa were taken from Gao et al. [20]

temperature of 280, 290 and 300 °C. Under flowing inert gas, the deviation is 2 °C at all positions. During the reaction, the temperature in the first part of the fixed bed is higher and decreases only slowly and is in total higher than under inert gas. Thus, if the temperature in the first part of the fixed bed is only slightly higher than under inert gas, the temperature at the other positions will only slightly deviate from the temperature in the first part (Fig. 7 right, e, f). The conversion curves coincide since the temperature measured in the first part of the fixed bed is representative for the temperature of the whole fixed bed (Fig. 7, left). With increasing temperature difference between fixed bed and heating block, the deviation of the other positions from the first position increases (Fig. 7 right, d), so that the temperature in the first part of the fixed bed is not representative for the temperature of the whole fixed bed any more.

Fig. 7 left shows besides the measurements with a catalyst mass of 75 mg also the measurement with a catalyst mass of 200 mg, dilution of 1:9 and temperature measurement in the middle of the reactor. Since the modified residence time τ_{mod} was kept constant, the conversions coincide at low conversions. As expected, after reaching the light-off temperature with 200 mg catalyst, a significant deviation occurs with a drastic influence on the conversion. A kinetic fit of the conversion curve with 200 mg catalyst would hence lead to incorrect parameters. Thus, avoiding light-off behavior should have first priority.

For the measurement with 75 mg catalyst, light-off behavior cannot be observed even at $m_{\text{SiC}}/m_{\text{cat}} = 9$. Different explanations are possible: with 200 mg catalyst, the distribution of catalyst and inert material could be inhomogeneous in the fixed bed. In an area of high catalyst density, high heat evolution could lead to a light-off phenomenon. In addition, the heat evolution with 200 mg catalyst is much higher at the reactor inlet. Due to the constant modified residence time τ_{mod} , the volumetric

flow rate is higher for 200 mg catalyst. If segments of the fixed bed with the same volume are compared, the residence time in these segments is much smaller with 200 mg catalyst than with 75 mg catalyst. Due to the smaller residence time, the conversion achieved in the segments is smaller. Hence, the reactant concentration at the reactor inlet is for 200 mg catalyst larger, and the higher reaction rate due to the higher heat evolution could lead to a light-off phenomenon. A quite similar explanation is given by Schüler and Hinrichsen [17]. The observation of an increasing maximum fixed-bed temperature with increasing volumetric flow rate is explained by a higher reaction rate at a smaller residence time.

Discussion

Experimental indication for light-off phenomena

Since the temperature for the experiment with 200 mg catalyst was measured in the middle of the fixed bed, the hotspot could not be detected. Only by slowly increasing the temperature, a light-off phenomenon could be observed. An abrupt conversion rise at a small temperature rise of the heating block (T_1) can be a first evidence of a light-off phenomenon. If the abrupt conversion rise is not accompanied by an abrupt rise of the fixed-bed temperature (T_2), it can be assumed that the thermocouple is at the wrong position. The actual evidence is to decrease the temperature in small steps after the abrupt conversion rise. If the conversion shows a hysteresis, i.e., the conversions are at the same temperature in the cooling cycle larger than in the heating cycle, it can be assumed that a light-off phenomenon occurs.

To assure that the observed hysteresis can be related to an ignition/extinction phenomenon, the modified residence time can be varied. According to the measurements with different catalyst mass shown in Fig. 7 and the temperature profiles at different modified residence times (Fig. 5), a lower modified residence time (higher flow rate) should result in a higher hotspot and facilitate the light-off. This is in contrast to what is common for technical reactors. In the case of technical fixed-bed reactors, a decreasing modified residence time leads to a decreasing hotspot temperature and a shift of the hotspot to a higher fixed-bed depth (z) [21, 22]. If the flow rate is increased, the local conversion in the beginning of the fixed bed decreases due to the lower residence time. The lower conversion leads to a higher reactant concentration in the beginning of the fixed bed. In a lab reactor, the higher reactant concentration with increasing flow rates leads to a higher reaction rate, which results in a higher heat production. The higher heat removal due to the higher flow does not compensate the higher heat production [18]. Thus, the hotspot in the beginning of the fixed bed increases with increasing flow rate. In a technical reactor, the conversion in the beginning of the fixed bed is usually low due to the long fixed beds and the higher flow rates. Hence, the concentration of reactants in the beginning of the fixed bed is usually high and the reaction rate should be less sensitive towards the flow rate than in a lab reactor. Thus, the hotspot shifts to a higher fixed-bed depth in the case of a technical reactor.

It should be mentioned that the same behavior in lab reactors was observed in other investigations. In a wall-coated micro reactor during ethylene oxidation, Lange et al. observed a hotspot formation at the beginning of the catalyst coating [23]. This hotspot was always at the beginning of the catalyst coating and did not shift to the reactor outlet with increasing flow rate.

Moreover, the temperature of the hotspot increased with increasing flow rate in this system [24]. The same phenomenon was observed by Schüler and Hinrichsen [17] who also monitored a higher hotspot temperature with increasing flow rate in a lab-scale fixed-bed reactor.

Besides modified residence time variations, measurements with different dilution ratios of catalyst with inert material are possible to check if a light-off phenomenon occurs. With increasing dilution ratio, the abrupt conversion rise at the heating cycle and the hysteresis at the cooling cycle should disappear, because the heat production is spread over a larger fixed-bed volume with a larger cooling area.

In the case that a light-off phenomenon seems to exist, different options are available. As radial conduction to the reactor wall is the most important influence in removing the heat from the fixed bed [3], it is reasonable to reduce the reactor diameter first. In many cases, the diameters of lab reactors are already small and a further reduction would lead to disturbing bypassing effects. Thus, the dilution of the catalyst with inert material is a good alternative. As discussed, lower flow rates will reduce the hotspot in lab reactors, thus low flow rates are favorable to avoid a light-off. But during kinetic measurements, different conversions have to be adjusted and the desired conversion dictates the flow rate at a given catalyst mass. A suitable way to achieve low conversions at low flow rates is to reduce the catalyst mass.

Position of the thermocouple in the fixed bed

Besides the experimental method described in Sect. “[Experimental indication for light-off phenomena](#)”, a well-positioned thermocouple can help to diagnose a deviation from isothermal behavior. Especially at pressures higher than atmospheric pressure and exothermic reactions, one should think about the right position of the thermocouple. In the literature, the thermocouple is nearly exclusively inserted against the direction of flow at the reactor outlet [3, 5, 8]. In the case of an isothermal fixed bed, this is the best choice, since the temperature is everywhere the same, and the thermocouple has only a small influence on the fluid dynamics at this position. However, runs 1–3 (Fig. 2) show that it cannot be assumed that the fixed bed is isothermal, even though measures have been taken to ensure isothermality, e.g., high dilution with inert material and small reactor diameter. Also Weatherbee and Bartholomew [25] realized in their work on the methanation of CO₂, that their data was probably not obtained under isothermal conditions, even though the reactants were diluted with 95% N₂. Since the thermocouple was positioned at the outlet of the fixed bed, they assume that the measured temperature was considerably smaller than the temperature at the reactor inlet.

In order to check for isothermality, the temperature in the first part of the fixed bed should be measured, even though inserting the thermocouple in the first part of

the fixed bed can have a more distinct effect on the fluid dynamics. However, since the temperature usually exerts a larger influence on the conversion than bypassing effects, securing isothermality should have first priority [5]. If there is only a small deviation between the fixed-bed and the heating-block temperature, a small temperature gradient also across the reactor can be assumed. For a small temperature gradient, the temperature only slowly decreases along the fixed bed (Fig. 7, right). This behavior is also observed in the simulation of hotspots during the hydrodesulfurization of thiophene ($\Delta H_R^\circ(298\text{ K}) = -147\text{ kJ mol}^{-1}$), a reaction with a standard enthalpy of reaction similar to the one of the methanation of CO_2 . At a reactor diameter of 6 mm, the fixed-bed temperature rises abruptly for about 6 °C and decreases slowly afterwards [26]. Thus, for a small temperature gradient the temperature in the first part of the fixed bed can be seen as representative for the temperature of the whole fixed bed, even if the fixed bed is not strictly isothermal.

Conclusions and outlook

An experimental approach for identifying deviations from isothermal conditions in lab-scale fixed-bed reactors with the use of only one single thermocouple is presented. Although the absence of deviation from isothermality cannot be excluded 100%, it is a strong justification to assume isothermality. Other techniques to verify isothermality like multiple-point thermocouples, fiber Bragg grating sensors, thermography measurements at optically accessible reactors or simulation studies are rarely used, because they imply either higher time requirements, expensive equipment or lack of appropriate equipment for small lab-scale reactors. Therefore, we propose the following purely experimental procedure if the other techniques are not available or applicable:

- (A) The measurement of the fixed-bed temperature should be close to the inlet of the fixed bed.
- (B) Compare the measured fixed-bed temperature for the chosen reactant feed composition with the measured temperature when an inert gas is flowing through the fixed bed. If the deviation is in the range of a few degrees, the occurrence of a hotspot is unlikely.
- (C) Increase the volumetric flow rate to see if the temperature increases. If this is the case, the occurrence of a hotspot at the reactor inlet can be assumed.
- (D) Increase the temperature step-wise (heating cycle) under the chosen conditions and then subsequently decrease it step-wise (cooling cycle). If no fluctuations and/or hysteresis of measured conversions occur, an absence of light-off phenomena is most likely.
- (E) Take action: If the experimental procedure points to the presence of a hotspot, reduce the reactor diameter until the lower limit is reached ($10 \approx$ reactor diameter/particle diameter [3]), increase the dilution with inert material and reduce the catalyst mass.

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