Heterogeneous Catalysis in Flow Reactors with Mass Transfer Effects: Propene Hydrogenation as a Model Reaction

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The goal of this TP is to utilize diagnostic tests (Madon-Boudart) to determine presence/absence of mass and heat transfer limitations in a packed bed reactor under various reactions conditions. Once the appropriate conditions have been found to remain within the kinetic regime (no heat and mass transfer limitations), the true kinetics of the reaction can be measured. The hydrogenation of propylene over a heterogeneous catalyst (Pt/TiO_2) will be used as a model system.

MAIN TARGETS

- Becoming familiar with the preparation of heterogeneous catalysts and their characterization
- Determining the presence/absence of mass/heat transfer effects for various operating conditions in a PFR
- Measurement of catalytic activity in a gas phase flow reactor

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1. INTRODUCTION

1.1 Heterogenous catalysts

Due to their thermal stability and their compatibility with flow processes, heterogeneous catalysts are usually preferred over homogeneous ones in industry. Among those, supported metal catalysts[1] (dispersed metal nanoparticles inside a porous support) form a major family of catalysts and tremendous efforts were spent to achieve a good level of understanding of those complex systems.

1.2 Mass transfer limitations in heterogenous catalysts

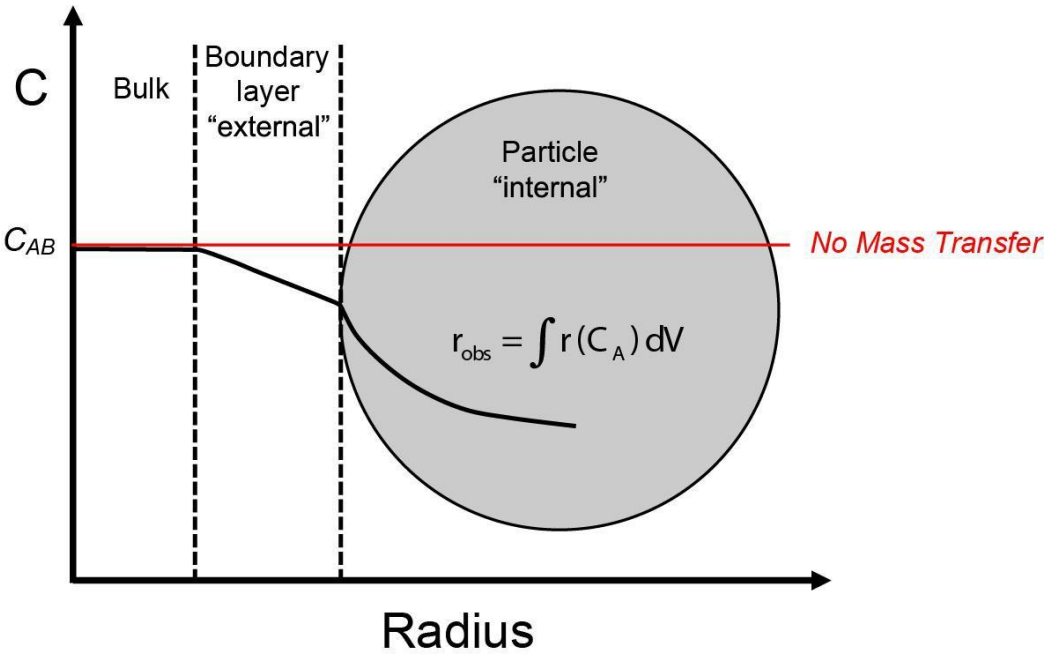

Figure 1. Illustration of external and internal mass transfer limitations in a spherical catalyst pellet

Despite the advantages of heterogeneous catalysts, the rate of reactions are usually lower than those of homogeneous catalysts. While this is partly due to metal dispersion (ratio of surface to total atoms) reducing the amount of catalytic sites, heterogeneous catalysts also frequently run into mass transfer limitations. As reacting molecules have to actually diffuse onto the catalyst surface in order to react, the surface concentration of reactants is different from the bulk concentration (Figure 1). In cases where the surface reaction rate is high relativeto the rate of diffusion in the bulk fluid, the surface concentration becomes lower than the bulk concentration, and the observed rate of reaction approaches the rate of diffusion of reactant to the catalyst surface. Mass transfer limitations can be further exacerbated in porous catalysts, where slow diffusion of reagent into the pores of the catalyst matrix results in concentration gradients within the catalyst pellet. These two cases are termed external and internal mass transfer limitations, respectively. Mass transfer limited reactions are typically not ideal, as the catalyst is not being fully utilized, and

are typically observed with increasing temperature (ask yourself: how does the rate of diffusion change with temperature relative to the rate of reaction?).

The Madon-Boudart test[2] is a way to determine whether the measured catalytic activity is being affected by transport effects, or is actually the true reaction rate. The test stipulates that for the catalyst to be free of transport limitations, the ratio of the rate of reaction to the concentration of the active metal must be constant throughout different metal concentrations. This criterion is known as Koros- Nowak (KN) criterion[2]. The active metal loading can be varied by diluting a catalyst with an inert material (must have similar diffusional characteristics to the catalyst), or by directly preparing catalysts with different metal loadings (Figure2). However, when using the latter option, caution must be taken to ensure each catalyst has similar dispersion in order to avoid effects of active site structure on reaction rate.

$$KN\ criterion\text{:}\ \frac{Rate\ of\ reaction}{Concentration\ of\ active\ metal} = Constant$$

This test can be further extended by plotting the logarithm of the reaction rate ($mol.s^{-1}.g_{cat}^{-1}$) vs the surface concentration of the active metal. A slope of 1 indicates that reaction is free of transport limitations for the reaction conditions used. Based on theory presented in the original Madon-Boudart publication, the value of the slope can not only indicate the presence/absence of heat and mass transfer but can provide insight into which types of heat and mass transfer are dominant (see Section 1.4).

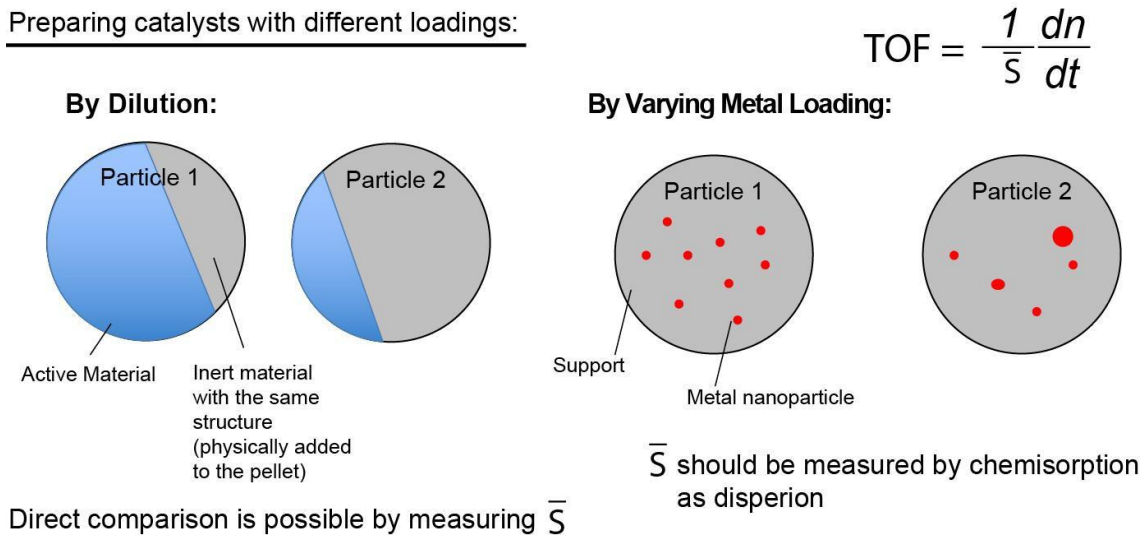

Figure 2. Different methods for producing catalysts of varying metal loading for the Madon-Boudart

1.3 Determination of mass transfer limitations in plug-flow reactors

Due to concentration gradients along the length of plug-flow reactors (PFR), reaction rates cannot be directly measured unless the system is operated in a differential manner[2] (< 10% conversion). Therefore, to determine the KN number by plots of reaction rate vs. surface concentration of active metal as mentioned above,

the reactor needs to be operated differentially. Alternatively, another method can be used to determine the absence/presence of heat and mass transfer limitations in a PFR that does not require differential operation (but does not allow for allow for calculation of the KN number). For the KN-criterion to be satisfied, conversions (X) over a range of active space time velocities (ρ) (moles of reagent per second flowing through the reactor normalized to the number of active sites) must be equivalent for catalysts with varying metal loadings. In other words, if X vs 1/ρ plots obtained from catalysts with different loadings coincide, it means that the KN-criterion is obeyed.

$$Space - velocity = \frac{Molar\ flow\ rate\ of\ the\ reactant}{weight\ of\ the\ catalyst} = \frac{n_0^-}{w_{cat}} \quad (2)$$

$$f_m = \frac{moles\ of\ active\ site}{w_{cat}} = \frac{mol\ (SA)}{w_{cat}} \quad (3)$$

$$\rho = \frac{n_0^-}{w_{cat}.f_m} \quad (4)$$

1.4 Investigation of types of heat/mass transfer limitations

In cases where KN-criterion is not obeyed, *i.e.* the system is under the influence of heat/mass transfer limitations, further analysis has to be made in order to understand what type of heat/mass transfer limitations are present in the system. In this aspect, slope (s) of ln(Reaction rate) vs ln(f_m) curves can be used to understand the nature of the mass transfer limitations that are present in the system[2]. s = 1 means that KN-criterion is obeyed, $0.5 \leq s \leq 1$ means that there are small internal mass transfer limitations, s = 0.5 means that there are severe internal mass transfer limitations, $0 < s < 0.5$ means that there are both intraphase (external) and interphase (internal) mass transfer limitations. Finally, s = 0 means that there are significant external mass transfer limitations since the reaction rate becomes totally independent of catalyst loading (f_m).

If the investigated reaction is exothermic, the value of s can be greater than 1 as well. s > 1 suggests that the system is suffering from both internal mass and heat transfer limitations. Lastly, in an exothermic reaction, there are two possible cases that can yield s = 1. In the first case s can be equal to 1 when the KN-criterion is obeyed. However, in the second case, s can be equal to 1 if internal heat transfer limitations that increase reaction rates perfectly mask the decrease in reaction rate caused by mass transfer limitations. Therefore, for exothermic reactions, one can say that KN-criterion is only obeyed if ln(Reaction rate) vs ln(f_m) curve yields s = 1 at two different reaction temperatures[2].

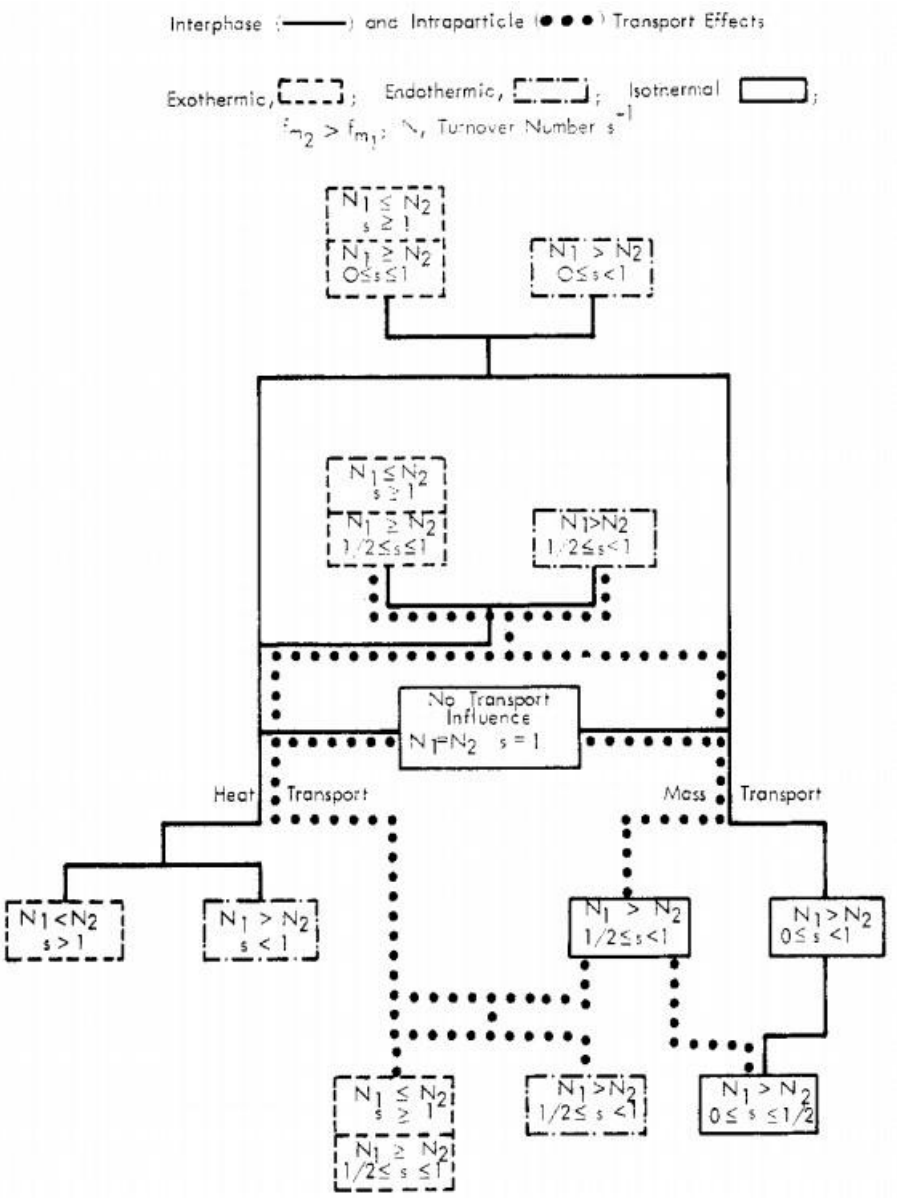

Figure. 3. Interphase and intraparticle transport effects. The chart indicates the trend of the turnover numbers N_1 and N_2 when $f_{m2} > f_{m1}$ and shows limits for the values of s when interphase and intraparticle effects exist separately or are coupled together. f_m is the active metal concentration and s is the slope obtained from the plot of ln rate vs ln f_m. Reproduced from Madon and Boudart.[2]

1.5 Synthesis of Pt/TiO_2 catalysts

Typically, students would prepare the catalysts used in this study. However, due to time limitations, catalysts were pre-synthesized this year.

Pt/TiO_2 catalysts of varying platinum loadings (0.1 wt% and 0.2 wt%), were prepared via a traditional wet impregnation of TiO_2 (Acros P25): Aqueous precursor solutions were prepared, containing the right amount of H_2PtCl_6 (10 mL of water per gram of catalyst) for the corresponding targeted metal-loading of the catalysts. After stirring for 2 minutes, the pre-calcined TiO_2 (500°C, 5h) was added. After stirring at room temperature for

1 hour (200 rpm), temperature was increased to 50 °C and the slurry was stirred for removal of excess of water. The catalyst was then dried overnight in an oven at 110 °C, calcined in static air (350 °C, 3h) and reduced overnight at 300°C under H_2 flow (30 mL/min) before experiments. The dispersion for each of the catalysts was measured by chemisorption (see Section 1.6 for chemisorption theory). Sieves canbe used to test the effect of catalyst pellet size.

1.6 Catalyst characterization by chemisorption of probe molecules

Chemisorption implies the formation of a bond between the probe molecule and the substrate, typically H_2 or CO on a transition metal. An adsorption isotherm is usually fitted using the Langmuir adsorption model[5] that considers the probe as an ideal gas (Fig. 2). When the adsorption stoichiometry of the probe molecule to substrate sites is known, the amount of surface sites can be determined. For instance, carbon monoxide adsorbs selectively on the surface metal atoms of Pt nanoparticles with a 1 : 1 CO : Pt stoichiometry. Hence, a sample containing 100 mol of Pt which adsorbs 20 mol of CO will have a metal dispersion of 20 % (80 mol of Pt are in the bulk of the NPs). The same reasoning applies to H_2.

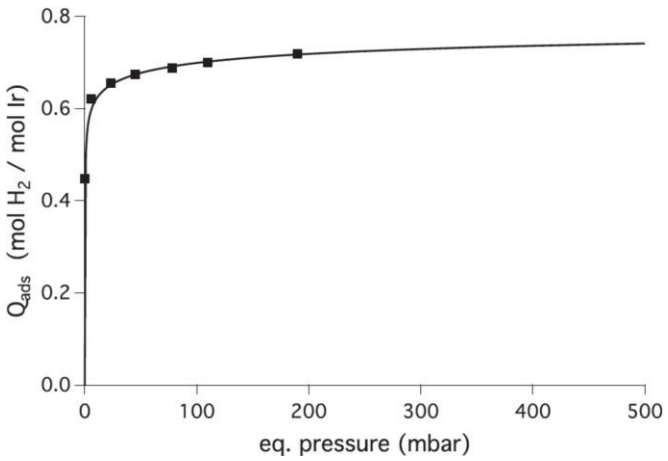

Figure 4. Typical H_2 adsorption isotherm

1.7 Propene hydrogenation as a model system

Catalytic hydrogenation reactions are one of the most important reactions that are used to reduce organic compounds in the chemical industry[3]. For instance, production of vitamin K, vitamin E and hydrogenation/semi-hydrogenation of vegetable oils proceed *via* catalytic hydrogenation reactions[3]. In this TP, gas phase hydrogenation of propylene will be used as a model to study the kinetics of hydrogenation reactions over a Pt/TiO_2 catalyst. This reaction was also selected as a model as it is exothermic (ΔH = -124 kJ/mol**)** and has extremely fast kinetics and is therefore subject to heat and mass transfer limitations.

$$C_3H_6 + H_2 \leftrightharpoons C_3H_8 \quad (5)$$

2. OBJECTIVES

The objectives of the present work are:

- *Determination of mass/heat transfer limitations.* Determine the presence/absence of heat/mass transfer limitations for propene hydrogenation over a Pt/TiO_2 catalyst using the Madon-Boudart test.

- *Measurement of catalytic activity in a gas phase flow reactor.* If heat/mass transfer limitations can be neglected for the chosen reactor conditions, kinetic data can be collected (turnover numbers, activation energy etc.).

3. EXPERIMENTAL

3.1 Safety

Safety goggles and lab coats are mandatory. Gloves are required when handling dangerous chemicals (*e.g.* acidic solution of H_2PtCl_6). Cryo-gloves are required to handle liquid nitrogen. Thermal gloves are required when working with hot glassware. Respiratory masks are required when handing fine powders. Fume hoods are available for the manipulation of dangerous chemicals. The TP is performed in an engineering research lab, high pressures and temperatures are used. A safety tour will be provided by the assistant for each group to identify safety procedures.

Hydrogen and propene are explosive. Before every run on the reactors, a leak test should be performed with an inert gas such as helium. Proper connection of the reactor outlet to ventilation should be checked.

3.2 Experimental setup

Catalytic activity will be tested in a flow reactor (Figure 4a). The system is complex and will be described in great details by the assistant during the first session. Shortly, the system can be divided into 3 units:

1) Feed of gas reagents
2) Catalytic reactor
3) Analysis by online gas-chromatography (Agilent 8860)

In Figure 4a, pressure regulators labeled A, B, and C are used to set the inlet pressure of hydrogen (H_2), helium (He) and propylene (Pe) to the reactor system, respectively. Do not change these pressures without permission from your teaching assistant. High pressures (> 20 bar) in the reactor system can lead to rupture disk failure. Downstream of the pressure regulators are two mass flow controllers (section E), that can be used to control the flow rate of two gases simultaneously. The two gases mix in part F (IMPORTANT: DO NOT MIX AIR AND HYDROGEN IN THE REACTOR SYSTEM). Subsequently. a three-way valve (section G) is used to divert the gas mixture to the furnace (H), where the catalytic reactor is located, or to the reactor-bypass loop (section D). Finally, the gas mixture can be sent to the GC, the vent or the bubble flow meter (J) by using the valves in section I.

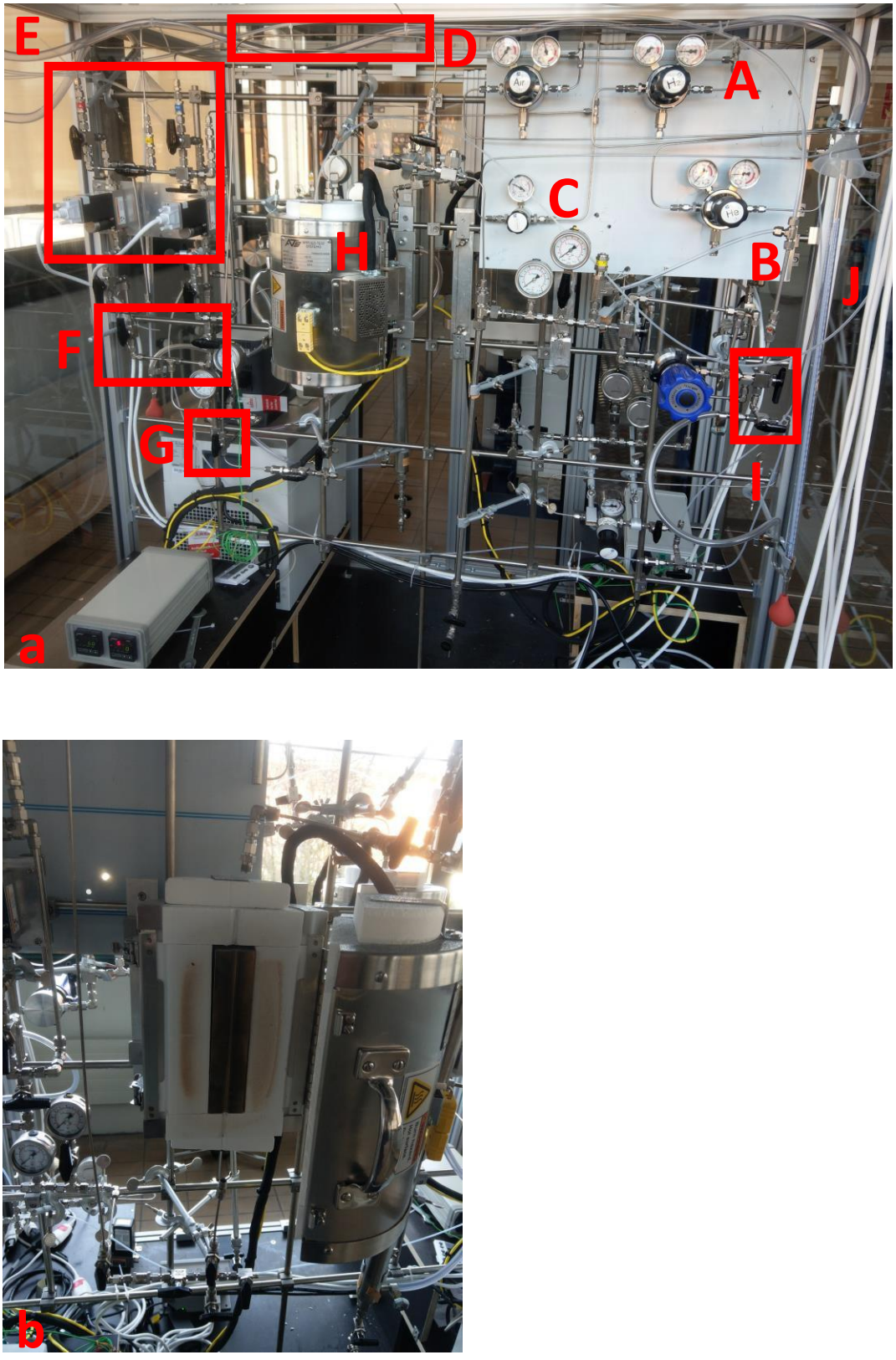

Figure 5. (a) Schematic view of the catalytic testing unit (b) Inside view of part H represent in Figure 4a.

3.3 Reactor packing

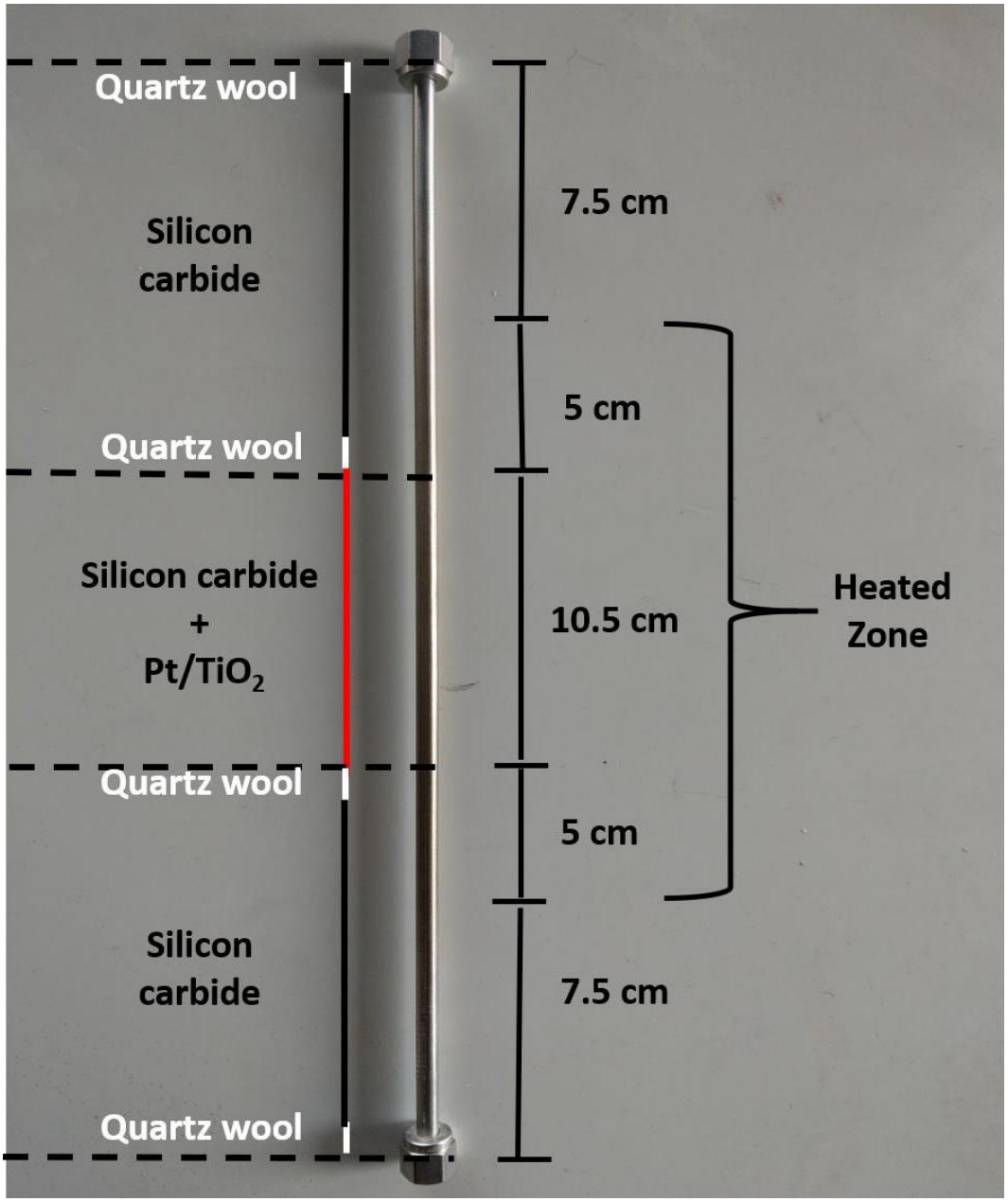

Figure 6. Illustration of tubular reactor packing.

Figure 6 illustrates the packing of the tubular reactor. The length of the PFR is 36 cm and will be cut from ¼" stainless steel tubing with an inner diameter of 4.572 mm. For each reaction 10-30 mg of catalyst will be loaded into the reactor. An inert powder with high thermal conductivity (silicon carbide, 150 um pellet diameter) will be used to dilute the catalyst in the center portion of the reactor as illustrated below. The remainder of the reactor will be filled with silicon carbide, using pieces of glass woolto separate the reaction zone. The reaction zone is placed 5 cm away from the boundaries of the heating zone to ensure isothermal operation. As a rule of thumb thediameter of reactor should be more than 10x larger than the catalyst pellet size to avoidnon-ideal flow patterns (i.e. bypassing of the catalyst).

$$\frac{Reactor\ diameter}{Pellet\ diameter} > 10 \quad (6)$$

References

(1) De Jong, K. P. *Synthesis Of Solid Catalysts*; Wiley-VCH Verlag GmbH & Co. KGaA, 2009.

(2) Madon, R. J.; Boudart, M. Experimental Criterion for the Absence of Artifacts in the Measurement of Rates of Heterogeneous Catalytic Reactions. *Ind. Eng. Chem. Fundam.* **1982**, *21* (4), 438–447. https://doi.org/10.1021/i100008a022.

(3) W. Bonrath, J. Medlock, J. Schütz, B. Wüstenberg, T. Netscher, Hydrogenation in the Vitamins and Fine Chemicals Industry—An Overview, in: I. Karamé (Ed.), Hydrogenation, InTech, Rijeka, 2012, pp. 69–90.(3)

(4) Boudart, M. Catalysis by Supported Metals*. In *Advances in Catalysis*; D.D. Eley, H. P. and P. B. W., Ed.; Academic Press, 1969; Vol. 20, pp 153–166.

(4) Boudart, M. Turnover Rates in Heterogeneous Catalysis. *Chem. Rev.* **1995**, *95* (3), 661–666. https://doi.org/10.1021/cr00035a009.

(5) Langmuir, I. THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. *J. Am. Chem. Soc.* **1918**, *40* (9), 1361–1403. https://doi.org/10.1021/ja02242a004.

Reminder

The lead group is responsible for planning the experiments to be done and must inform the backup groups of their duties and experiment plan in due time.

For the first session, the following schedule is proposed:

- Presentation of the subject / set-up by the assistant 30 min
- Individual study of the manipulation by the student 2 h
    - Schematic representation of the set-up
    - Work plan
    - Mass and heat balances applied for the study have to be developed and presented to the assistant in the afternoon of the 1st day.
- Discussion with the assistant 30 min
    - Definitive work plan
- Reactor Operation Remainder of day

WARNING

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At the end of the work, the installation must be cleaned and free of products. The report will not be corrected until everything is clean! If necessary, a negative point will be added to the final mark.

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