

Report Re-Invitation Grant for Research Alumni

First, I would like to thank the International Scholars & Welcome Office (ISCO), since this Re-Invitation Grant was a great opportunity to reunite with my former working group and to explore other research fields at KIT.

My name is Karin Walter Bahamondes, former PhD student at the Chemistry Faculty at KIT in the group of Prof. Dr. J.-D. Grunwaldt, where we do research in the field of heterogeneous catalysis. I did my PhD between 2012 and 2016 in the topic Catalytic Synthesis of Higher Alcohols. After finishing my PhD, I returned to my home country, Chile, and started working on a field new to me: Water treatment for industrial processes at Hidrolatina de Chile Spa. In this company I am part of the R&D area, where we attempt to solve water-related issues for several process industries, mainly in the mining sector.

Therefore, the aim of my visit was two-fold. On the one hand, I got in contact with other Institutes at KIT, whose working fields are closer to my current work in Chile. On the other hand, I planned the experiments and prepared the catalysts for future experimental work for the group of my host, Prof. Dr. J.-D. Grunwaldt, which could lead to a publication. Therefore, my report is divided into two parts.

Visit to other Institutes at KIT and THE Heidelberg

Through ISCO I contacted Irma Mantilla from the Institute of Eco-Industrial Development (IEDE) to discuss about participating in the Chile-KIT Cluster as an industrial partner. This would make Hidrolatina part of a database of companies, which could potentially cooperate with universities involved in this project.

In parallel, through Prof. Dr. Grunwaldt, I got in contact with Prof. Dr. Horn and Dr. Saravia from the Water Chemistry and Water Technology Institute and Prof. Dr. Wilhelm from the Institute of Technical Chemistry and Polymer Chemistry. Both groups are currently working in topics close to our interest at Hidrolatina. In this context, the 30th of September I did a presentation entitled "Hidrolatina's perspective on Reverse Osmosis" (Figure 1) in the EBI-building, where students and members of both research groups and also our working group attended. The presentation included a summary of our company's history, mission, vision, working fields and the research projects under development. It was a fruitful discussion, where we exchanged our opinions regarding reverse osmosis.

In addition, I visited the laboratories of Prof. Dr. Wilhelm's group in company of Christoph Pfeifer and Christian Fengler (both PhD students), where we discussed their current approach to desalination using hydrogels.



Figure 1: Presentation at EBI-building.

The group of Prof. Dr. Grunwaldt organized an excursion to HTE in Heidelberg (Figure 2), where I was also invited to participate. Dr. Schunk and Dr. Schulz-Dobrick presented the company's strategy and an example of how HTE solves problems through high throughput experimentation. We also visited their laboratories guided by HTE workers. We finalized the visit with a dinner together in Heidelberg, where we could exchange our opinions and interests.



Figure 2: Excursion to THE, Heidelberg.

Experimental work in Heterogeneous Catalysis: Continuous synthesis of higher alcohols

During my PhD thesis I designed and built a downward-flow trickle-bed reactor for the continuous synthesis of higher alcohols from synthesis gas and ethanol using copper-based catalysts. Later on, the reactor was upgraded with online analytics to measure the products of the reaction (gas and liquid). During my stay in Karlsruhe, the online analytics were being calibrated in the frame of a master thesis. I cooperated with this task by helping with the development of a calibration methodology and the supervision of the master student with Dr. Saraçi.

The initial plan of my stay was to perform experimental work in the trickle-bed reactor, but, unfortunately, the reactor did not pass the leakage test, which is extremely important when using CO as reactant. The reason of the failure was the malfunctioning of the backpressure regulator, which had to be sent for repair to the manufacturer. Therefore, my work was centered more in planning the experiments and preparing the catalysts for them.

To design a trickle bed reactor, there are not only construction and safety aspects that have to be regarded, an important part of the proper-functioning of this particular reactor is related to the method of packing, catalyst wetting, axial mixing, channeling and mass and heat-transfer limitations.

In my previous work, we theoretically ensured a trickle-flow and decided us for the dry packing method following the criteria presented by Mary et al. [1]. Additionally, we decided to use SiC as inert material to ensure proper axial mixing, catalyst wetting and helping with the heat transfer within the catalyst bed. Assumptions that we verified theoretically (for further details see [2]). A critical aspect, that was pending from my PhD thesis, was to experimentally prove the absence of mass-transfer limitations. Catalytic reactions have to face external and internal mass-transfer steps to proceed. External mass-transfer accounts for the diffusion of reactants (or products) from the bulk/stagnant layer limit to the surface of the catalyst particle (and backwards for products). Internal mass-transfer includes the

diffusion of the reactants (or products) within the catalyst particle from the external surface of the catalyst to the active phase (and backwards for the products). Therefore, two types of experiments have to be performed to ensure the absence of mass-transfer limitations. [3]

Test A: Internal mass-transfer limitations

This test measures the conversion (CO and ethanol) for different particle sizes at a constant space velocity. The reactions conditions are planned to be: 320 [°C], 80 [bar], $n_{\text{EtOH}}:n_{\text{CO}}=0.3$, $\text{CO}:\text{H}_2:\text{N}_2=0.4:0.4:0.2$, total flow of 500 [ml/min], 1.5 [g catalyst], catalyst:SiC (0.21 [mm])=1:1 and 5 [cm] of catalyst bed. For performing these experiments, catalysts in different particle sizes (0.20-0.25 [mm], 0.45-0.50 [mm] and 0.80-1.0 [mm]) were prepared by wet impregnation of copper and zinc nitrate precursors on Al_2O_3 . Al_2O_3 was previously calcined at 500 [°C] for 5 hours. After the impregnation, the catalysts were calcined at 350 [°C] for 5 hours. Later on, the catalysts were doped with 1 [mol%] of Cs (precursor: CsCOOH) also by wet impregnation and then again calcined under the same conditions (for further details see [2]).

The expected result of this test is a graph as the one presented in Figure 3. From this graph a particle size which ensures a kinetically-controlled regime will be chosen. This type of regime should be assured when studying the kinetics of a particular reaction, because the reaction rates are not falsified by diffusion and can only be attributed to the catalytic reaction itself.

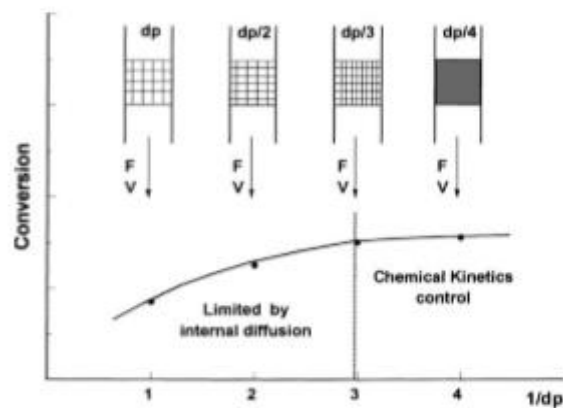


Figure 3: Experimental test to evaluate internal mass-transfer limitations in catalytic reactors. [3]

Test B: External mass-transfer limitations

This test measures the conversion (CO and ethanol) for a established catalyst particle size using different bed volumes and the corresponding total flow to ensure a constant space velocity (Table 1). For performing Test B a compromise had to be taken, according to the previously mentioned calculations [2], the minimum reactor length should be 5 [cm] (proper axial mixing) and the isothermal zone of the reactor was 11.5 [cm] long (isothermal zone of ± 5 [K]). To maintain the isothermal zone was of greater importance for us, therefore we decided to decrease the length of the reactor bed. The reactions conditions to be used are: 320 [°C], 80 [bar], $n_{\text{EtOH}}:n_{\text{CO}}=0.3$ and $\text{CO}:\text{H}_2:\text{N}_2=0.4:0.4:0.2$.

Table 1: Conditions for testing external mass-transfer limitations.

Reactor volume [ml]	Volumetric flow [ml/min]	Catalyst bed length [cm]	Space velocity, LHSV [L (STP)/vol cat h]	Catalyst mass [g]
8.0	500	10.0	3750	3.0
4.0	250	5.0	3750	1.5
2.7	167	3.3	3750	1.0
2.0	125	2.5	3750	0.75

The expected result of this test is a graph as the one presented in Figure 4. As in the previous graph, to perform kinetic studies, the reactor should be operated with conditions that ensure no limitations by external diffusion, i.e. a kinetically-controlled regime.

The future plan is to perform these experiments, when the reactor is operative again. When the data is collected, the limitations of the reactor can be evaluated and proper reactions conditions for the synthesis of higher alcohols from synthesis gas and ethanol using Cu based catalysts can be chosen, which might lead to studies related to the kinetics of this particular reaction. This procedure will also enable to establish a methodology for testing mass-transfer limitations for this particular reactor.

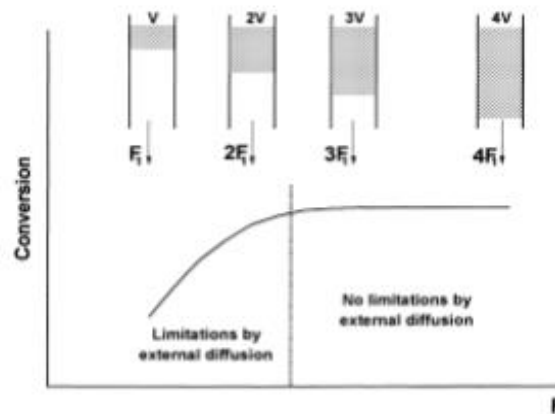


Figure 4: Experimental test to evaluate external mass-transfer limitations. [3]

Conclusions

In summary, visiting KIT again was a very enriching experience. It was a good opportunity to further work on research in catalysis, but also an opportunity to build new links that might come to cooperation in future.

References

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- [3] C. Perego, S. Peratello, Experimental methods in catalytic kinetics, Catal. Today, 52 (1999) 133-145.