

# Theory & Computational Catalysis (Probabilistic Analysis of Single Particle Temporal Analysis of Products Microreactor)

Renato Feres<sup>1</sup>, Gregory S. Yablonsky<sup>1,2\*</sup>, Xiaolin Zheng<sup>1</sup>, John T. Gleaves<sup>1</sup>

<sup>1</sup>Washington University, St. Louis, Missouri 63130 (USA)

<sup>2</sup>Saint Louis University, St. Louis, Missouri 63103 (USA)

\*gregoryyablonsky@yahoo.com (corresponding author)

## Introduction

The procedure to extract intrinsic reaction rates for chemical transformation over catalyst particles from reaction-transport data for a thin-zone Temporal Analysis of Products (TAP) microreactor has been previously introduced by Shekhtman, et al [1]. In accordance with this procedure, catalyst kinetic characteristics (apparent kinetic constants, substance storages, and time delays) are obtained in the course of multi-pulse experiments and presented as functions of catalyst composition. The thin-zone TAP reactor (TZTR) is a very useful special case of the previous three-zone TAP reactor configuration, in which the thickness of the catalyst zone is made very small in comparison to the entire reactor length. Having a very thin catalyst zone makes the change in the gas concentration across the catalyst zone small compared to its average value. A key advantage of the TZTR is that the catalyst bed can be changed uniformly by exposing the catalyst to a long series of small pulses at a conversion of up to 80% (it is much higher than in a differential PFR) [2]. Recently, a new configuration of the TZTR was proposed in which the reaction zone is collapsed to the surface of a single micron-sized catalyst particle in a bed of inert quartz particles [3]. The particle occupies less than 0.3% of the cross-sectional area of the microreactor, so that the reaction zone can be considered a point source. In a typical experiment, the microreactor was packed with approximately 100,000 inert quartz particles (210-250  $\mu\text{m}$  in diameter) and a single Pt catalyst particle (300-400  $\mu\text{m}$  in diameter) usually positioned in the middle of the reactor bed. An advantage of this configuration is that concentration and temperature gradients in the catalyst bed can be assumed to be negligible for very fast catalytic reactions even in the domain of high conversions. The probabilistic theory and experimental validation of the TAP-experiment over a single catalyst particle modeled in two dimensions is presented in this paper [4].

## Materials and Methods

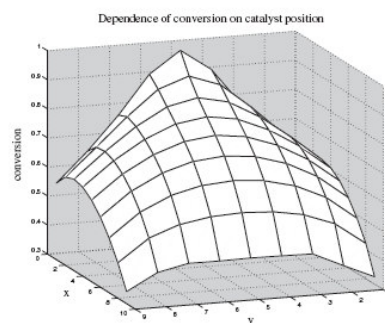
The probabilistic theory describes a single pulse-response experiment, which is similar to the single pulse Temporal-Analysis of Products (TAP)-experiment. The analysis is based on the general theory of Brownian motion with “killing” and the Feynman-Kac formula. Different diffusion-reaction problems, particularly the problem of “diffusion-very fast reaction” (infinite rate reaction) have been analyzed. In the latter case, the probability for a reactant to be converted equals a purely geometric characteristic, namely, the probability for a reactant molecule to hit at least one catalyst particle in a configuration of particles. Solving a boundary value problem, the probability of conversion can be found as a function of the apparent kinetic parameter. Based on experimental data on exit flow and conversion, this parameter can be extracted.

## Results and Discussion

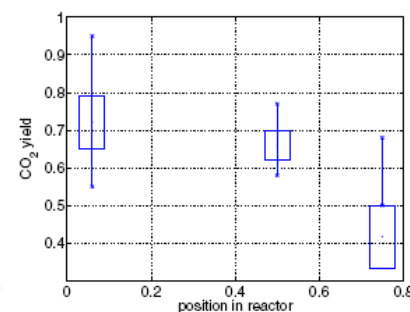
Experimental data in studies of CO oxidation over a single particle of Pt foil catalyst show a qualitative agreement with data from computational experiments based on the developed probabilistic theory. This comparison was made based on conversion of CO at different catalyst positions in the TAP microreactor. CO conversion was found to be the greatest when the catalyst particle is placed near the microreactor entrance due to the transport

properties of the CO molecules in the reactor. In the Knudsen diffusion regime, the diffusivity of each gas in the mixture is independent of the composition of the mixture. When the catalyst particle is placed near the reactor inlet, there is a greater probability for CO (reactant) molecules to keep returning near the catalyst particle due to random (Brownian) motion caused by multiple collisions with the inert particles in the packed reactor bed. As the catalyst particle is moved closer to the reactor outlet, the probability that a CO molecule will come back and hit the catalyst particle once it has passed the position where the catalyst is located decreases. The nature of the random motion is important in explaining both the relatively high yield for a single catalyst particle and the way the yield is dependent on catalyst position. Random motion creates the opportunity for the molecule to return multiple times to where the catalyst is located, but the number of returns decreases if the distance between the position of the catalyst particle and the reactor outlet decreases.

In computations for two-particle catalyst configurations, it was found that a non-trivial dependence of the reactant conversion on some geometric characteristics, especially the distance between particles. A distance was found for which conversion is highest [4].



**Figure 1.** Computational result of conversion as a function of catalyst position.



**Figure 2.** Comparison of theoretical and experimentally obtained CO<sub>2</sub> yield/CO conversion for single catalyst particle for 3 different locations in microreactor.

## Significance

The probabilistic theory based on Brownian motion presents an explanation for gas molecule behavior in the TAP microreactor under the Knudsen diffusion regime. It also provides an initial starting point to solve boundary value problems for a more realistic TAP reactor geometry (3-dimensional) and study multi-particle configurations in a more systematic way.

## References

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