

## High Throughput Catalysis (Non-Steady-State Catalytic Activity Characteristics using TAP-studies)

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### Introduction

The new approach for high throughput monitoring of non-steady-state catalytic characteristics is based on the combination of a new catalyst preparation technique, which combines in a single apparatus an atomic beam deposition (ABD) system with a temporal analysis of products (TAP-2) reactor system, and a new methodology of non-steady-state kinetic characterization. The approach is focused on establishing direct, reproducible correlations between changes in surface composition and changes in catalyst activity. Catalyst samples were prepared by directly adding metal atoms in sub-monolayer amounts to the surface of micron-sized particles. The method is illustrated by the examples of CO oxidation over a series of Pd/PdO catalysts and hydrocarbon selective oxidation over modified VPO catalysts. The Pd deposits were characterized using XPS, SEM and TEM as well. CO<sub>2</sub> production during TPR experiments exhibited oscillatory behavior related to the self-assembly of the catalyst micro-structure. For VPO-catalysts, the different concentrations of chosen metallic modifiers (Te, Co) are compared and the best one is determined.

### Materials and Methods

'State-by-state' catalyst kinetic screening of catalytic properties is illustrated by the example of hydrocarbon selective oxidation. For many substances of the reactive mixture (butane, furane, butadiene, maleic aldehyde, aldehyde, CO<sub>2</sub>, CO), intrinsic catalytic properties, i.e. apparent kinetic constant of substance transformation, apparent time delay, apparent storage, were determined as functions of controlled oxidation/reduction degree. Non-steady-state characterization was performed using pulse response methods and temperature-programmed reaction (TPR). Based on the systematically obtained characteristics, the hypotheses on the detailed mechanism and its dependence on the catalyst state are proposed.

### Results and Discussion

Methodologically, the non-steady-state kinetic catalyst characterization procedure is based on the application of the idea to perform the TAP-experiment in thin-zone reactors. A

thin-zone TAP-reactor (TZTR) proposed in 1999 is a very useful special case of the three-zone TAP-reactor configuration, in which the thickness of catalyst zone is very small compared to the reactor length. Having the catalyst zone very thin making 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 values of conversion up to 80% (It is much higher than in the differential PFR).

New results in theory of TZTR are presented, particularly the method for extracting chemical transformation rate from reaction-diffusion data with no assumption on the kinetic model ("kinetic model-free procedure"), so called Y-procedure. The mathematical foundation of the Y-procedure is a Laplace-domain analysis of two inert zones in TZTR followed by transposition to the Fourier domain. When combined with time discretization and filtering, the Y-procedure leads to an efficient method for determining the reaction and reaction rate in the active zone. Using the Y-procedure the concentration and reaction rate of a non-steady catalytic process can be determined without any pre-assumption regarding the type of kinetic dependence. The Y-procedure can be used to relate changes in the catalytic reaction rate and kinetic parameters to changes in the catalyst surface composition.

### Significance

The developed approach can be considered as a framework of high throughput non-steady state catalytic activity characterization. Particularly, on the basis of this approach the advanced software for non-steady state kinetic data interpretation can be developed.

### References

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