

**ASSESSING THE INTERPLAY OF SPATIAL AND TEMPORAL
UNCERTAINTIES IN THE CATALYST STATE DURING TEMPORAL ANALYSIS
OF PRODUCTS (TAP) KINETIC EXPERIMENTS**

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The kinetics of catalytic reactions are typically correlated to certain descriptors of the catalyst state, such as the concentrations of surface intermediates or the number of accessible active sites. However, these kinetics as well as catalyst descriptors are always subject to experimental uncertainties due to the finite rates of transport processes within experimental kinetic devices and the limited accuracy of analytical techniques. We have employed numerical modeling and statistical analysis to assess the interplay between spatial and temporal uncertainties in the context of Temporal Analysis of Products (TAP) experiments.

Keywords: *heterogeneous catalysis, chemical kinetics, Temporal Analysis of Products (TAP), uncertainty metrics, state-defining and state-altering experiments*

INTRODUCTION

Accurate measurements of chemical reaction rates, i.e. quantitative kinetic experiments, provide an essential source of information for fundamental and applied studies in heterogeneous catalysis. Examples of research tasks that necessitate high-quality kinetic data range from falsifying rival hypotheses about a dominant mechanism of a catalytic reaction, to benchmarking *ab initio* calculations, to engineering efficient and safe industrial process. Furthermore, mathematical models of catalytic reactions and reactors are stimulating research subjects themselves, as vividly presented in Marin, Yablonsky, and Constales (2018) [1]. Temporal Analysis of Products (TAP) is a unique methodology for

precise, time-resolved kinetic characterization of heterogeneous catalytic reactions [2]. TAP research has inspired the development of a new, general approach to kinetic characterization—*chemical calculus*—which rests on the following pillars:

- 1) **Well-defined transport** of gas provides a reliable standard process against which the reaction kinetics can be accurately measured. In TAP experiments, such a process is provided by Knudsen diffusion.
- 2) **The local spatial uniformity** of the catalyst state at the relevant length scale is maintained at a high level (i.e. low spatial uncertainty) during the kinetic experiment. In a Thin-Zone TAP Reactor (TZTR), this is ensured by making the catalyst layer thin with respect to inert beds.
- 3) The kinetic experiment does not perturb the state of the catalyst, i.e. **infinitesimal change** of state during a state-defining measurement. The nanomolar sizes of TAP pulses facilitate this condition, given that the catalyst loading and the concentration of relevant sites are suitable.
- 4) **Well-defined alteration** of the catalyst state between its natural limiting states is implemented by accumulating infinitesimal changes in series. Multipulse TAP experiments can alter the catalyst state between, for example, fully reduced and fully oxidized (limited by the vacuum stability of relevant surface species).

Careful evaluation of experimental uncertainties associated with and validity ranges of various assumptions required by these pillars has become an integral part of the continuously evolving mathematical apparatus of "*chemical calculus*" [3]. Two aspects of uncertainty are typically discussed in the TAP literature. The degree of spatial uniformity of the gas and surface concentrations within the catalyst (Pillar 2), which is controlled by the geometric factors and the interplay of reaction kinetics and diffusion. Another aspect of uncertainty is the degree to which a single measurement affects the catalyst state (Pillar 3). Shekhtman et al. [4] demonstrated that a TZTR maintains a high degree of catalyst uniformity (low spatial uncertainty) for a wide range of per-pulse conversions and that the kinetic models can be effectively linearized for small changes of the catalyst state during state-defining experiments. Capitalizing on both types of uniformity, TZTR analysis stimulated the development of the moment-based (i.e. time-averaged) method of Shekhtman reactivities as well as the fully time-resolved Y-Procedure [5]) that extract kinetically "model-free" catalyst characteristics from the TAP data. Finally, the Rate Reactivity Model (RRM) have been formulated [6] to further unravel the mechanistic information contained within the Y-Procedure derived "model free" concentration-rate-uptake transients. However, spatial and temporal uncertainties have not been evaluated within a single mathematical framework to date.

Undoubtedly, precise kinetic characterization of catalytic materials within a flexible model like RRM could have a significant impact on the science of catalysis, which motivates the development of adequate kinetic devices and data interpretation practices for the task. A suitable device should ideally balance two commonly counteracting objectives: (1) to be relevant for "real world" non-ideal behaviors of practical catalytic systems and (2) to satisfy the assumptions involved in decoupling transport and kinetic phenomena from experimental data. Therefore, future extensions as well as practical applications of the RRM in particular and, in a wider context, of the TAP-inspired "*chemical calculus*" require a more general measure of the uncertainty involved in kinetic measurements. Herein, we propose a general formalism for quantifying separately the spatial and temporal aspects of

the uncertainty of the catalyst state. Although introduced and exemplified for a typical TAP experiment, the proposed measures of uncertainty can accommodate a much wider scope of kinetic experiments and data interrogation tactics.

FORMULATION OF THE PROBLEM

To introduce the problem, let us consider the practical context of a typical TZTR experiment: an experimenter encounters a new catalytic sample with unknown properties and needs to optimize the conditions of exploratory TAP measurements. Uncertainties abound. A few routine control experiments can be used to demonstrate that experiment is firmly supported by the first pillar of “*chemical calculus*” (i.e. $F(t) \sim F_{SDC}(t)$ for an inert and $D^2 \sim T/M$). Support from the second and third pillars are less readily found. The experimenter must choose the pulse size, the mass and position of the catalyst sample within the reactor, the composition of the gas mixture, temperature, settings of the mass-spectrometer, etc. Some of those choices are made based established practices, prior experience, or common sense outside the scope of this manuscript. The choice of the catalyst loading, however, is intimately related to goal of minimizing uncertainty. From one perspective, the less catalyst is used, the thinner the catalytic zone can be made, resulting in a lower spatial uncertainty of the catalyst state. From another perspective, the more catalyst is used, the smaller fraction of free active sites that will be irreversibly altered by the experiment, resulting in lower temporal uncertainty of the catalyst state. We postulate that there exists a range of realistic parameters where these two different aspects of uncertainty are at a non-trivial interplay and can be balanced to satisfy different criteria within the experiment. The main objectives of this work are to (i) define a general framework that can delineate the spatial and temporal aspects of the catalyst state uncertainty, (ii) exemplify this framework with synthetic data within a wide range of experimental parameters. Importantly, the framework should account for the information from the entire transient, rather than the final state only. This is relevant for experiments with reversible processes, wherein essential non-uniformities can temporarily develop during the experiment.

FORMULATION OF THE MODEL

The standard 1D model of a TAP experiment was used to prepare synthetic data. The transport and reactions of gas within a contiguous pseudo-homogeneous domain obey the following equation:

$$\varepsilon_l \frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} + \rho_{cat,l} R_l(C, S)$$

where ε is porosity, D [m^2/s] is the gas diffusivity, $\rho_{cat} = m_{cat}/V_l$ [kg_{cat}/m^3] is the amount of catalyst within the zone volume, and R [$mol/kg_{cat}/s$] is the gas transformation rate.

At the reactor exit ($x=L$), a boundary condition is imposed to reflect the non-reversible nature of gas pump-out by the vacuum system:

$$C(L, t) = 0$$

At the reactor entrance, the boundary condition reflects the time-dependent flux of gas molecules injected into the reactor—usually a sharp pulse approximated by a Dirac delta-function or a Gaussian:

$$-AD \frac{\partial C}{\partial x}(0, t) = N_p \delta_{t-0^+}$$

where N_p [mol] is the pulse intensity.

Gas-phase continuity is prescribed at the internal boundaries between quartz and catalyst zones for both concentrations and fluxes:

$$\begin{aligned} C(l_-, t) &= C(l_+, t) \\ -AD_{l-} \frac{\partial C}{\partial x}(l_-, t) &= -AD_{l+} \frac{\partial C}{\partial x}(l_+, t) \end{aligned}$$

The reaction term is set to zero inside the inert (quartz) zones, and it is given by a microkinetic or a general kinetic expression in the active (catalyst) zone. Concentrations of surface species S [mol/kg_{cat}] are governed by time-resolved equations:

$$\frac{\partial S_i}{\partial t} = R_i(C_i, S_i)$$

which are spatially defined only within the catalyst zones and assume that surface species do not transport in space explicitly on the length and time scales of the experiment.

Initially, before time zero, concentrations of gaseous substances are set to zero everywhere in the reactor, while the initial concentrations of surface species S_0 may be finite as a result of prior events within the system:

$$\begin{aligned} C(x, 0) &= 0 \\ S(x, 0) &= S_0 \end{aligned}$$

The experimentally observed quantity is obtained as the flux of gas across the exit boundary of the reactor domain:

$$E_{exp}(t) \sim F_{exit}(t) = -AD \frac{\partial C}{\partial x}(L, t)$$

This model was numerically solved using the Method of Lines (MoL), as implemented in the TAPFIT code [7]. Simulation results were post-processed with in house developed software.

UNCERTAINTY MEASURES

In order to analyze different aspects of the catalyst state uncertainty, we propose to consider the following quantities. Given a spatio-temporal distribution of a catalyst state descriptor $S(x,t)$, the spatial and temporal components of the total catalyst state variance, i.e. marginal variances, are given by

$$v_x = E[(S - S_x)^2] = \iint \omega(x)\nu(t)(S - S_x)^2 dxdt$$

$$v_{\tau} = E[(S - S_{\tau})^2] = \iint \omega(x)v(t)(S - S_{\tau})^2 dxdt$$

and the total variance is given by

$$v_{xt} = E[(S - S_{xt})^2] = \iint \omega(x)v(t)(S - S_{xt})^2 dxdt$$

The space- and time-averaged quantities are defined as:

$$S_x(t) = \int \omega(x)S(x, t) dx$$

$$S_{\tau}(x) = \int v(t)S(x, t) dt$$

$$S_{xt}(t) = \iint \omega(x)v(t)S(x, t) dxdt$$

with the weighing functions $\omega(x) = 1/L_{cat}$ and $v(t) = \lambda e^{-\lambda t}$. Here, λ is chosen to be equal to the total collection time of a single pulse-response experiment.

With these definitions, fractional contributions of the spatial and temporal factors into the total uncertainty of the catalyst state can be analyzed for a given experiment as

$$\Omega_x = \frac{v_x}{v_{xt}} \text{ and } \Omega_{\tau} = \frac{v_{\tau}}{v_{xt}}$$

RESEARCH ANALYSIS

Equipped with the aforementioned definitions, we explored how the fractional uncertainty measures behave as functions of various experimental factors. Four sets of TAP experiments were simulated in which the probe gas irreversibly reacted with the surface sites according to the first-order kinetics (see parameters in Table 1).

These four cases span different combinations of high/low values for the two critical dimensionless parameters of a TAP experiment: (1) the relative thickness of the catalyst zone L_{TZ}/L_r symmetrically positioned in the middle of the domain and (2) the relative amount of the probe gas molecules in a single pulse with respect to the total amount of surface sites available on the catalyst surface for reaction. Within each dataset, the rate constant was varied over three orders of magnitude to sample different conversions, while other parameters were kept constant. The fixed quantities included the catalyst's linear packing density in the reactor bed and the concentration of surface species per unit mass, as is typically the case in laboratory practice. The amount of catalyst loaded and the amount of gas molecules injected in the pulse were used as variable parameters. Figure 1 summarizes the analysis results.

As expected for the first order process, gas conversions in cases one and two are very similar, despite different pulse sizes. But fractional variances behave differently. In the first three cases, the temporal fractional uncertainty dominated the spatial uncertainty. Only for the case with a relatively thick zone ($L_{TZ}/L_r=0.2$) and a large catalyst number ($N_p/N_S=0.1$) do the fractional uncertainties reverse the order for large rate constants. Surprisingly, small state-defining pulses with ($N_p/N_S=0.001$) produce the same total variance for the thin and thick zones (cases 1 and 3, respectively), and this variance is independent of the rate constant. In the other two cases, as expected, higher conversions result in higher total variance, which for the last case reaches an order of magnitude higher value for the maximal rate constant.

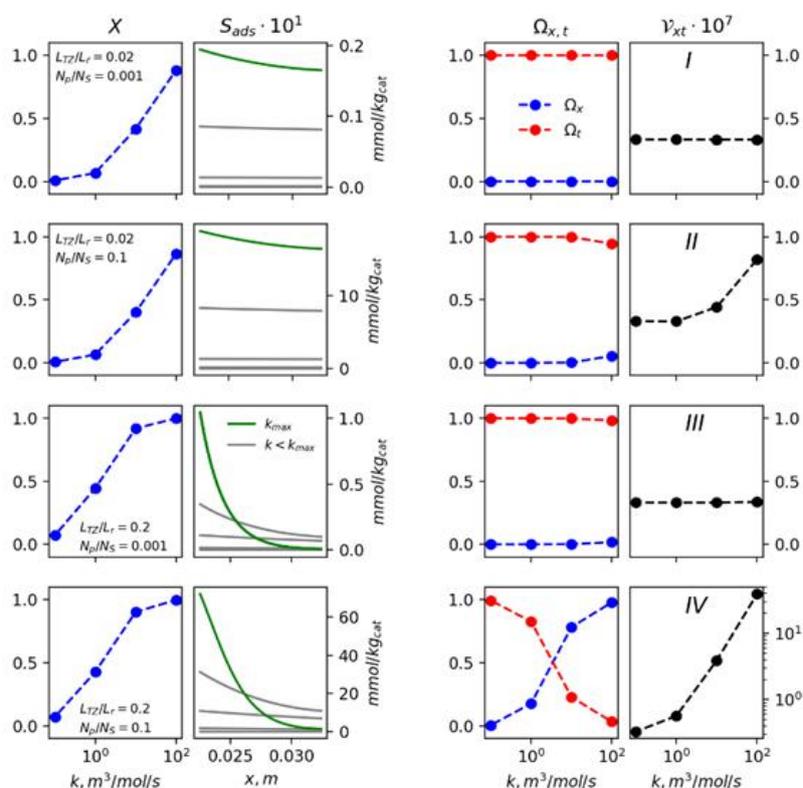


Fig. 15. Left to right on each row: gas conversions, adspecies concentrations, fractional uncertainties, and the total variance (right) of the catalyst state as functions of the rate constant for four sets of simulation parameters

Table 8. Simulation parameters

Reactor length, L_r	$50 \cdot 10^{-3}$ m	Linear packing density, ρ_{bed}	$10 \cdot 10^{-9}$ kg _{cat} /m (d 4mm)
Ne diffusivity at 273K, D	$2 \cdot 10^{-3}$ m ² /s	Total site density, $C_{S,tot}$	0.01 mol/kg _{cat}
Packing voidage, ϵ	0.4	R	$k(C_{S,tot} - C_S)C_G$

CONCLUSIONS

In conclusion, we proposed a new, more general mathematical framework for measuring the non-uniformity of the catalyst state in TZTR kinetic experiments. Importantly, the spatial and temporal components of the total variance can be analyzed separately. We illustrated the use of the new framework with numerically simulated TAP data, which suggest that the proposed uncertainty measures exhibit non-trivial behavior. Future extensions of this work will include sensitivity analysis of the uncertainty measures with respect to the choice of weighing functions and model parameters as well as analysis of the interplay between the spatial and temporal uncertainties. For example, the product $\Omega_x \cdot \Omega_t$ in the limit of a single catalytic site may yield useful insights into the micro/mesoscopic details of the catalytic process. We foresee that this framework will play an important role in the continually developing mathematical apparatus of “*chemical calculus*.”

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PROCESS SIMULATION AND LIFE CYCLE ASSESSMENT OF STEAM CRACKING PROCESS: EVALUATION OF THE IMPACT OF TECHNOLOGICAL IMPROVEMENTS BASED ON RELEVANT DATA OF THE COMPLETE INTEGRATED FURNACE PLATFORM

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МОДЕЛЮВАННЯ І ОЦІНКА ЖИТТЄВОГО ЦИКЛУ ПРОЦЕСУ ПАРОВОГО КРЕКІНГУ: ВИЗНАЧЕННЯ ВПЛИВУ ТЕХНІЧНИХ МОДИФІКАЦІЙ НА ОСНОВІ РЕЛЕВАНТНИХ ДАНИХ ПРО КРЕКІНГОВУ УСТАНОВКУ

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