

# INTERNET KINETICS: REMOTE CONTROL OF TEMPORAL ANALYSIS OF PRODUCTS (TAP) REACTOR SYSTEM

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## Summary

The Temporal Analysis of Products (TAP) reactor system has evolved from its original design based on molecular beam scattering experiments to a TAP-3 reactor system that allows the experimentalist to operate remotely from a computer all parts of an automated system. This configuration allows access to this unique catalyst characterization tool from all parts of the world. This abstract will highlight the experimental and technical capabilities of the remote control TAP-3 system by showing several key results and addressing automation design considerations to allow the system to be operated safely in the event of disruptions such as Internet/power outages.

## Keywords

Micro-reactors, Novel reactor technologies

## Introduction

Understanding how the catalytic activity and selectivity of a material is related to its composition and structure is a fundamental problem in the field of catalysis. Solving this problem requires finding relationships between kinetic data and structural data. Relationships that provide a link between reaction kinetics and the structure of the active catalytic site are important because they provide essential information for explaining how catalyst systems work, and for creating new or improved catalysts. To develop an activity-structure relationship for a gas-solid catalytic system, it is necessary to obtain kinetic data that can be directly related to the structure/composition of the solid catalyst, especially the catalyst's surface. For reactions involving industrial catalysts such as supported metals or mixed-metal oxides, acquiring kinetic data can be a challenge since the reaction kinetics and the catalysts are typically very complex.

The TAP reactor system<sup>1-3</sup> was developed to probe the catalyst kinetic characteristics in order to gain fundamental information on what the structure/composition of the catalyst may be. The TAP approach uses "interrogative kinetics (IK)<sup>2</sup>," which combines TAP vacuum pulse response experiments with atmospheric steady-state and transient experiments to characterize the activity of both technical and model catalysts over a wide domain of pressures ( $10^5$ - $10^6$  Pa) and relaxation times ( $10^3$ - $10^4$  s). The IK approach involves kinetic testing of a catalyst and

systematically altering its composition or structure in a well-defined process. After the catalyst composition is incrementally changed, its kinetic characteristics are measured and matched with the composition or structural change. The kinetic measurement is performed under non-steady-state conditions in such a way so as to not significantly alter the kinetic properties of the sample, and to give intrinsic kinetic information. The observed kinetics can be directly related with the observed composition change. The approach provides an experimental and theoretical methodology for determining the number of active sites on technical metal oxide catalysts, and a method for measuring the intrinsic kinetic properties of the active sites.

## Apparatus and Methodology

The TAP reactor system was first patented by the Monsanto Company in 1986 as a novel device for studying kinetics and mechanisms of heterogeneous catalyzed gas-phase reactions using a transient response technique with submillisecond time resolution<sup>1</sup>. Now more than 20 years later, it has undergone several design configurations to the state-of-the-art advanced TAP-3 reactor system which is a fully automated instrument that can be operated either locally or remotely via the Internet. This design allows researchers who did not have access to the TAP reactor to now have the ability to perform TAP experiments on their catalyst samples.

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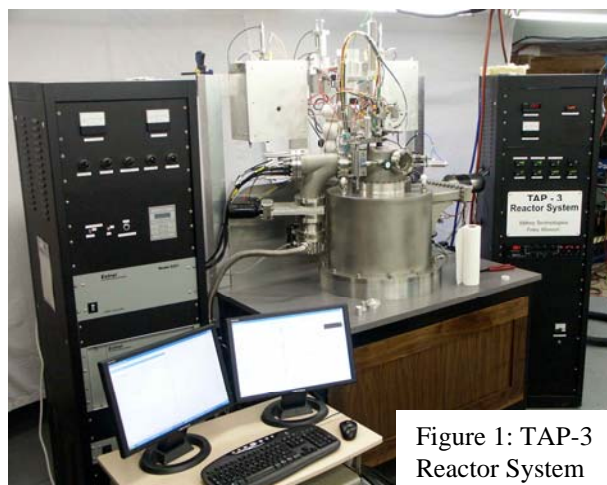


Figure 1: TAP-3 Reactor System

The TAP-3 reactor system (Figure 1) is comprised of (1) a pulse-valve manifold assembly that supplies gas reactants for pulsed and flow experiments at user defined temperatures and pressures, (2) a microreactor assembly that can be operated isothermally or in temperature programmed mode, (3) a mass spectrometer detector contained in a high-throughput ultra-high vacuum chamber, and (4) a computer based control and data acquisition system.

The TAP-3 menu of experiments includes, but is not limited to, high-speed vacuum pulse-response (TAP Knudsen pulse-response experiments, TAP pump-probe experiments, and TAP multipulse experiments, pulse experiments with a change of time within a pulse and between pulses), atmospheric pressure steady-state, step-transient, and SSITKA experiments, temperature programmed desorption (TPD), and temperature programmed reaction (TPR) experiments. In addition, newly developed software allows the user to create programmed experimental sequences, which can be stored in memory, and then performed automatically<sup>3</sup>.

## Experimental Applications of TAP-3

This paper will first review the system design and automation modifications that were performed so that the TAP-3 could be safely operated by a remote user through an Internet protocol. Two examples are provided in which remote users located at Texas A&M University and at CNRS in Lyon, France operated the TAP-3 using the remote control protocol to extract kinetic information using CO oxidation on Pt-based catalysts as a test reaction. The data collected in the remote mode was subsequently transferred for off-line analysis. These results demonstrate that safe, remote control operation of the TAP-3 is feasible, the results are transparent in terms of the originating source, and a new paradigm for collaboration on heterogeneous reaction kinetics is now possible.

Previous TAP remote control experimental results collected in St. Louis will also be highlighted, such as

furan oxidation over VPO catalysts to produce maleic anhydride (MA). From the TAP pulse response experiments, it was found that the activity and selectivity of the VPO catalysts improve significantly when the surface of the catalyst is oxidized by an atmospheric flow of oxygen prior to reaction with furan. Results of multipulse experiments indicate that there is an optimal oxygen surface concentration needed to yield a maximum in MA production. This occurs when the oxidized VPO surface is reduced by approximately 15 furan pulses (Figure 2). Another feature found from the non-steady-state experiments was that the maximum product yield of MA occurs at the lowest reactor temperature taken, 400 °C. Below 400 °C, the MA production decreases due to the decrease in the rate of reaction. These results are explained based on mechanisms with two types of active sites described in previous papers<sup>4</sup>.

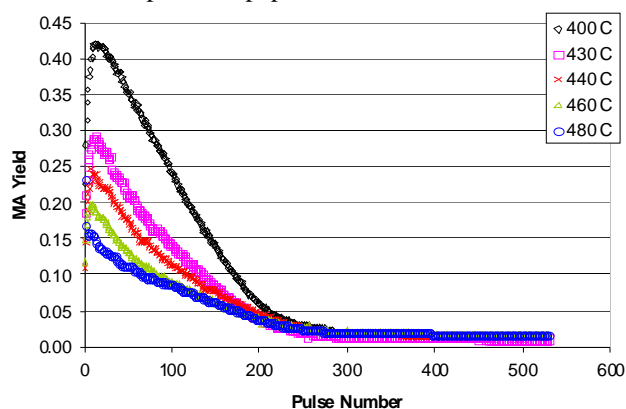


Figure 2: TAP vacuum pulse response data for MA yield as a function of the furan pulse number for reactor temperatures between 400 – 480 °C.

The above example is only one application of the TAP-3 reactor system to obtain kinetic data. The TAP-3 system has also been used to obtain kinetic characteristics of Pt powder<sup>5</sup> and Pt supported mesoporous and SBA-15 silica for the CO oxidation reaction to investigate support effects, reactant adspecies surface lifetimes using TAP pump-probe experiments, and activation energies of reactant adsorption/desorption and reaction. The most recent application of the TAP-3 reactor system has been to explore reactant adsorptions of CO and O<sub>2</sub> on gold supported catalysts.

## References

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