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## STEADY-STATE ISOTOPIC TRANSIENT KINETIC ANALYSIS (SSITKA)

In the study of reactions on heterogeneous catalysts over the past 40 years, much use has been made of transient kinetic techniques in order to provide insight into surface reaction processes and mechanisms. These techniques have typically employed at reaction conditions the use of stopping/starting the flow of one of the reactants or of pulsing the reactants. With the exception of experiments studying the exchange reaction between molecules at steady flow (1), it is difficult to extrapolate the results from these transient, non-steady-state studies to interpret the nature of surface reaction under steady-state conditions.

The steady-state isotopic transient technique developed by Happel et al. (2-4) and Biloen et al. (5) allows the monitoring of important kinetic parameters under steady-state reaction conditions. Experimentally the decay or development of isotopic species is monitored mass-spectrometrically at steady state after switching between reactant isotopes in the feed stream without perturbing the reactor pressure; a typical normalized isotopic transient is displayed in Fig 1. For a homogeneous surface reaction the rate can be written as

$$\text{TOF} = \theta / \tau ,$$

$\theta$  and  $\tau$  being the site coverage and average lifetime of reaction intermediates, respectively. Unlike conventional steady-state methods, SSITKA is able to deconvolute the reaction rate into contributions due to coverage of intermediates versus contributions due to the reactivity of the reaction intermediates. This ability is very powerful since it permits us to address the nature of groups of reaction sites. For SSITKA,  $\tau$ , the surface resident time, corresponds to the area under the normalized transient curve in Fig 1, a simplicity that can not be claimed by isotopic pulse methods (6). Barring readsorption, the pseudo-first order rate constant,  $k$ , is given by the reciprocal of  $\tau$ . The "steady-state surface concentration of reaction products and intermediates can be calculated by integrating the transient curves (after correction for gas-phase holdup) and applying the formula:

$$N_i(s) = (A) * (\text{rate of } i \text{ formation})$$

where  $A$  - the area under the normalized transient response curve. For conventional non-steady-state transient techniques (7), which attempt a similar decoupling of the reaction rate, the analysis is complicated by the pressure

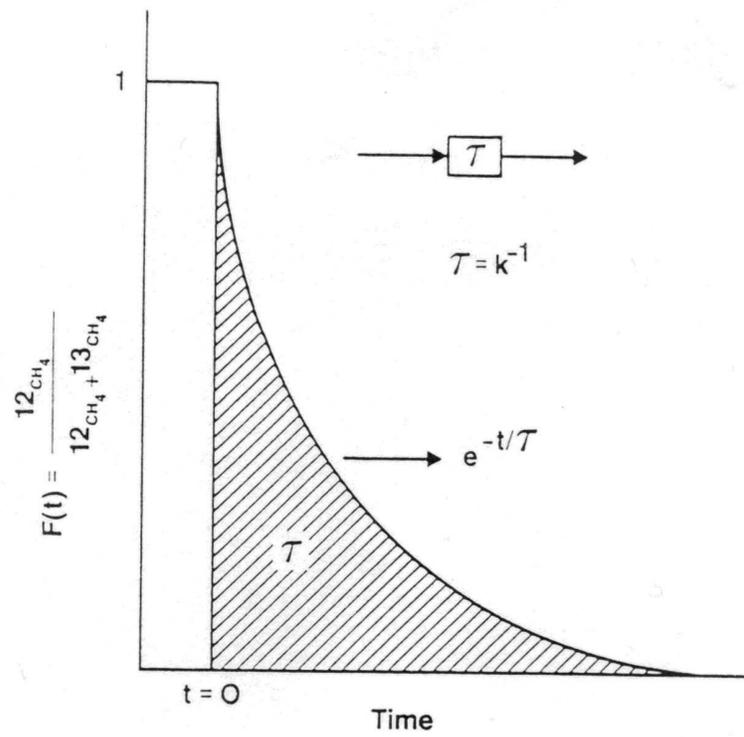


Figure 1: Typical Isotopic Transient

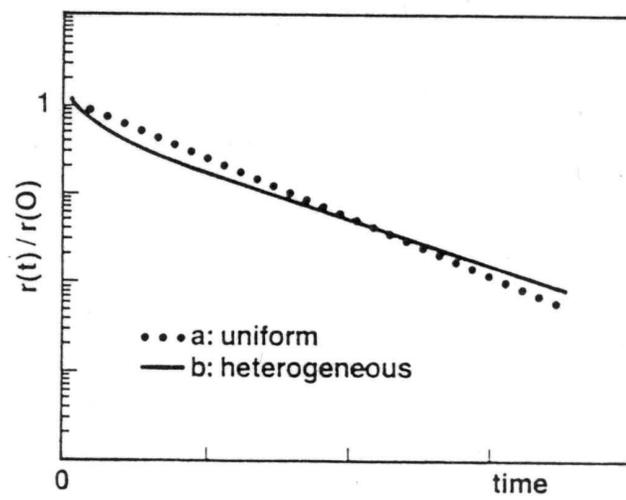


Figure 2: Observing Surface Heterogeneity

shock that transpires due to the depletion of reaction intermediates during the transient. Comparison of SSITK results to those from traditional non-steady-state transients for ammonia synthesis (8) and methane coupling (9) clearly show that the measurements made under non-steady-state conditions do not relate well to the situation existing under steady-state reaction.

Proper analysis of data acquired by SSITKA also permits one to quantify the heterogeneity of the surface. A semi logarithmic plot of the normalized isotopic transient data for a first-order reaction is expected to be linear. However, for a heterogeneous surface the semi log plot will show a curve convex to the origin (Fig 2). Consequently, a first-order surface reaction taking place on a nonhomogeneous surface can be modeled as a sum of exponentials, the parameters of which can be estimated by fitting the transient curve; i.e.,

$$\text{TOF} = \sum_i (\theta_0 x_i k_i \exp(-k_i t)),$$

here  $\theta_0$  and  $x_i$  are the initial fractional coverage and the fraction of the total coverage in the  $i^{\text{th}}$  pool of intermediates, respectively. Several deconvolution techniques have been developed to determine distribution functions of the site distribution from the transient equation above (10-11). Currently, the most powerful method is that developed by de Pontes et al. (12) which performs an inverse Laplace transformation of transient data to obtain an a-priori distribution function for  $k$ , and consequently for the strength of the sites. The relationship has the form

$$\text{TOF} = \theta_0 * \int (k e^{-kt} f(k)) dk,$$

the activity distribution function  $f(k)dk$  being the probability that the intrinsic activity lies between  $k$  and  $k+dk$ . This means that this method of analysis can be employed to determine reactivity constants for intermediate species that are formed along parallel, independent pathways. Thus, for the ammonia intermediates in the ammonia synthesis reaction over a Ru/silica catalyst, the bimodal distribution in Fig 3(b) was obtained following the addition of a K promoter to the catalyst (13). The presence of a second peak at higher activity indicates the creation of a set of very active reaction sites as a result of K promotion. The normalized area under each peak corresponds to the relative amount of ammonia intermediates on that type of site. For the ammonia synthesis over a commercial iron catalyst, Nwalor and Goodwin (14) recently presented a comparison of reactivity distribution functions based on the Temkin theoretical model and on the transformation method developed by de Pontes et al. (Fig 4). It was inferred that the apparent non-uniformity was derived from the basic structure of the surface rather than from adsorbate-induced surface segregation or aggregation. A fit of the Temkin model to the SSITK results yielded reasonable values for the Bronsted transfer coefficient, the active site density of the working catalyst surface, and a nitrogen adsorption affinity window that is commensurate with that implied by the a priori method of de Pontes et al.

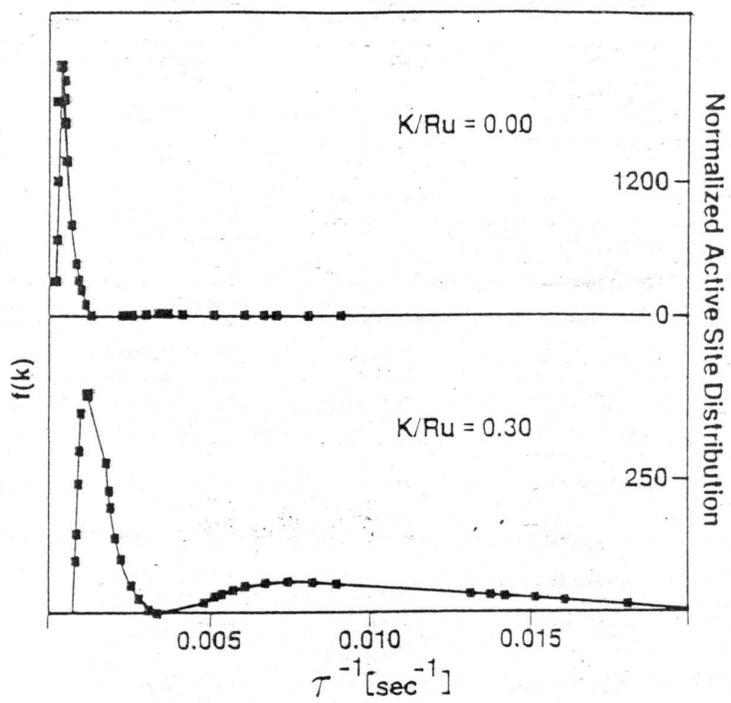


Figure 3: A Plot of  $f(k)$  for Ammonia Synthesis on (a) Unpromoted and (b) K-Promoted Ru/Silica

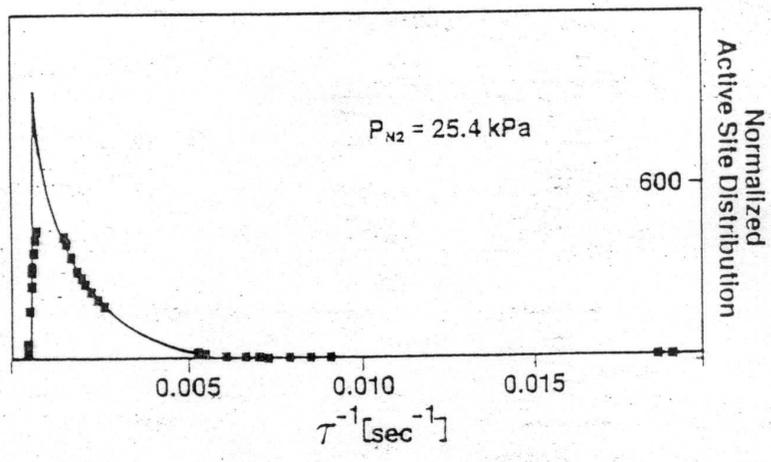


Figure 4: Comparison of Activity Distributions

Recent work in the laboratories of the University of Pittsburgh has demonstrated the usefulness of SSITKA for a wide variety of investigations of heterogeneously catalyzed reactions, including CO hydrogenation (15-16), CO oxidation (17), the oxidative coupling of methane (9,18-20), CO + NO reaction (17), ammonia synthesis (8,13-14,21), and the partial oxidation of propylene to acrolein (22). There also exists a significant body of literature reporting investigations employing SSITKA to study the mechanism of CO hydrogenation from Happel, Biloen, Sachtler, Belt, Bennett, Mims, Delgas, and their respective coworkers. SSITKA results have been reported additionally for a few other reactions such as benzene hydrogenation (23).

To date, all applications of SSITKA have been to gas phase reactions on solid metal and metal oxide catalysts. However, it would appear, based on calculations, to be applicable to some liquid phase and enzyme-catalyzed reactions, provide the catalyst is on a solid, resident phase in the reactor.

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