Overview of Steady-State Isotopic Transient Kinetic Analysis (SSITKA) for Catalysis

1. Background

In the study of reactions on heterogeneous catalysts over the past 40 years, much use has been made of transient kinetic techniques to provide insight into surface reaction processes and mechanisms. These techniques are typically employed using reaction conditions and involve stopping/ starting the flow of one of the reactants or of pulsing the reactants. However, 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.

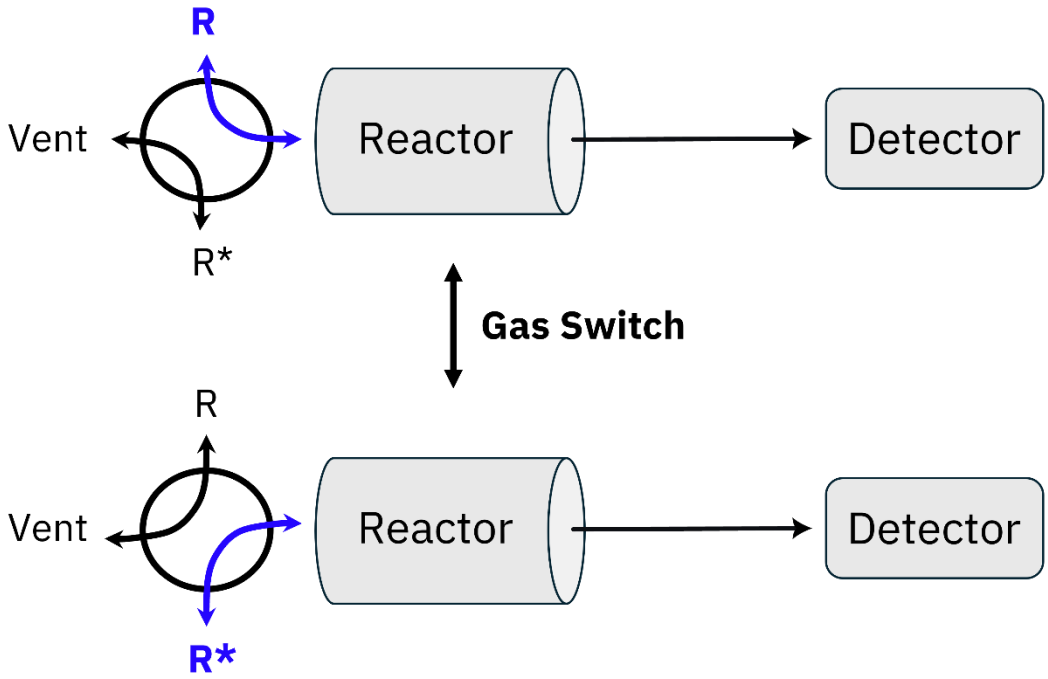

Figure 1: Schematic of typical SSITKA instrument setup

The steady-state isotopic transient technique developed by Happel et al.[1-3] and Biloen et al.[4] allows the monitoring of important kinetic parameters under steady-state reaction conditions, and the general schematic of the reaction system is shown in Figure 1. Experimentally the decay or development of isotopic species is monitored using mass-spectrometry at steady state after switching between reactant isotopes in the feed stream without perturbing the reactor pressure. 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.

2. SSITKA Theory

Consider a first-order irreversible reaction with non-isotopically labeled samples R → P shown in Eqn. 1. Once a steady state has been achieved, the isotope-labeled reactant is introduced (t = 0), and the isotopically labeled species replace the non-labeled species (Eqn. 2). After the reactant gas R is replaced with isotopic-labeled R*, any remaining non-labeled products P must have originated from the intermediate I present on the surface in steady-state before the switch. Therefore, the total amount of P is equal to the amount of surface species (N_i), assuming no isotopic effect on the reaction.

$$R \rightarrow X \rightarrow P \tag{1}$$

$$R^* \rightarrow X^* \rightarrow P^* \tag{2}$$

A typical normalized isotopic transient curve is displayed in Figure 2. For a homogeneous surface reaction, the turn-over frequency (TOF), or rate based on the number of active sites, can be written as:

$$TOF = \frac{\theta}{\tau} \tag{3}$$

Where:
θ = site coverage
τ = average lifetime of reaction intermediates, or surface resident time

For SSITKA, τ corresponds to the area under the normalized transient curve in Fig 1, a simplicity that cannot be claimed by isotopic pulse methods.[5] Barring readsorption, the pseudo-first order rate constant, k, is given by the reciprocal of τ. 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:

$$N_i\ (surf.) = A[rate\ of\ i\ formation] \tag{4}$$

Where:
N_i (surf.) = surface concentration of intermediate
A = the area under the normalized transient response curve

For conventional non-steady-state transient techniques, which attempt a similar decoupling of the reaction rate, the analysis is complicated by the pressure shock that transpires due to the depletion of reaction intermediates during the transient.[6] Comparison of SSITKA results to those from traditional non-steady-state transients for ammonia synthesis[7] and methane coupling[8] clearly show that the measurements made under non- steady-state conditions do not relate well to the situation existing under steady-state reaction.

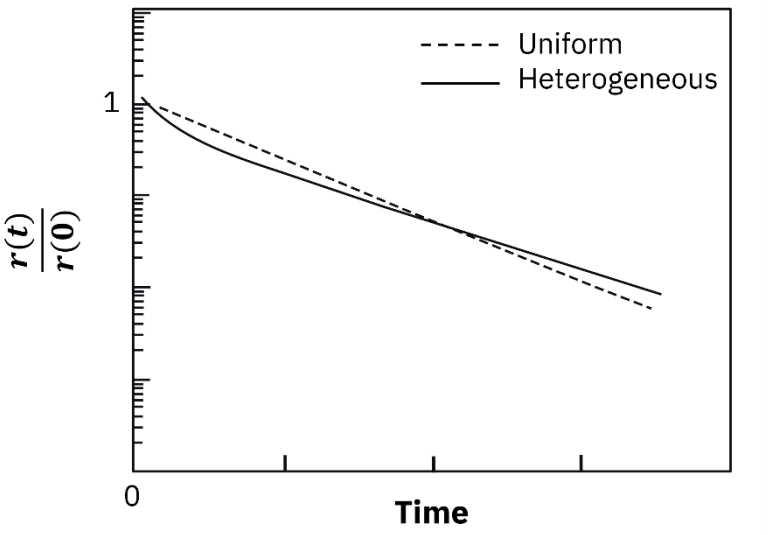

Figure 3: Observing surface heterogeneity

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.,

$$TOF = \sum_i \left(\theta_0 x_i k_i e^{-k_i t}\right) \quad (5)$$

Where:
θ_0 = initial fractional coverage in the ith pool of intermediates
x_i = fraction of the total coverage in the ith pool of intermediates

Several deconvolution techniques have been developed to determine distribution functions og the site distribution from the transient equation in Eqn 6.[9,10] Currently, the most powerful method is that developed by de Pontes et al.[11] 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:

$$TOF = \theta_0 \int \left(k e^{-kt} f(k)\right) dk \quad (6)$$

Where:
f(k)dk = the activity distribution function, or 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.

3. Experiment

The **AMI 300 SSITKA chemisorption analyzer** and **AMI Master400** mass spectrometer was used to characterize the adsorption of H_2 and D_2 on Pd/Al_2O_3 catalyst. The catalyst was pretreated with 50mL/min of 10% H_2/Ar mixture at 300°C for 1h, and then the sample was purged with Ar for 30 min to cool down to 155°C until the baseline was stable. For the SSITKA experiment, the total flow rate was 50mL/min (H_2 and D_2 10 mL/min, Ar 40mL/min, and the reaction temperature is 155°C. SSITKA of H_2 and D_2 was performed at atmospheric pressure.

4. Results

Initially, deuterium gas is pre-adsorbed on the surface of the catalyst. When deuterium and hydrogen were switched into the bed, isotope exchange occurred between the adsorbed deuterium and hydrogen, and the formation of HD was observed. At this point, HD generation begins to grow until it peaks and then drops rapidly in a short period of time. When the deuterium flow is turned off and the hydrogen flow is introduced, the opposite process is observed. This is consistent with H. Backman's conclusions and also verifies the H_2/D_2 isotope exchange reaction mechanism.[11] It was confirmed that H_2 and D_2 dissociated into surface H* and D* and reacted to produce HD. This can also be used to reveal the basic steps of hydrogen on the surface of noble metal catalysts, such as adsorption, dissociation, and recombination, which are the cornerstone of all complex catalytic reactions involving hydrogen (e.g., hydrogenation, dehydrogenation).

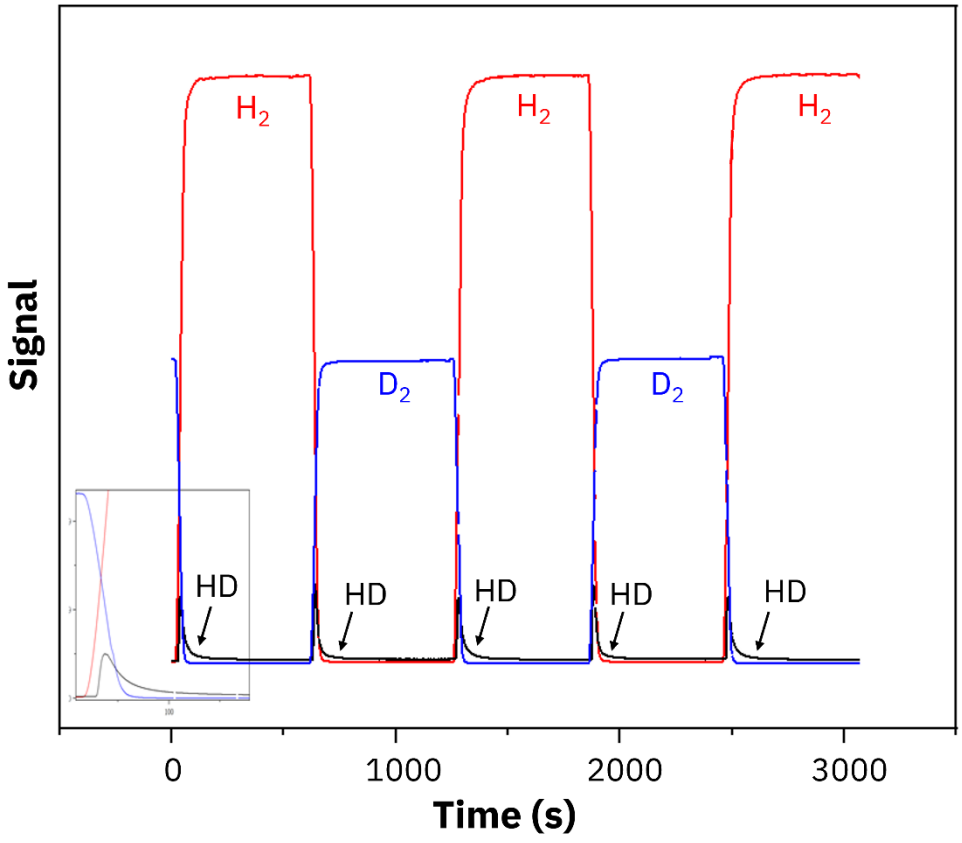

Figure 4: H_2-D_2 switching SSITKA experiment of Pd/Al_2O_3 catalyst

5. Conclusions

The dynamic process of HD signal generation (rapid rise to peak and then fall) is confirmed to follow the dissociation-recombination mechanism at the microdynamic level. The complete primitive steps of hydrogen adsorption, dissociation and recombination on precious metal catalysts are intuitively revealed, which provides a direct experimental basis for more complex hydrogen-related hydrogenation and dehydrogenation catalytic reaction mechanisms. The **AMI 300 SSITKA** paired with the **AMI Master400** mass spectrometer provided accurate, reliable information for H_2/D_2 SSITKA experiments, shown in Figure 5.

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, provided the catalyst is on a solid, resident phase in the reactor.

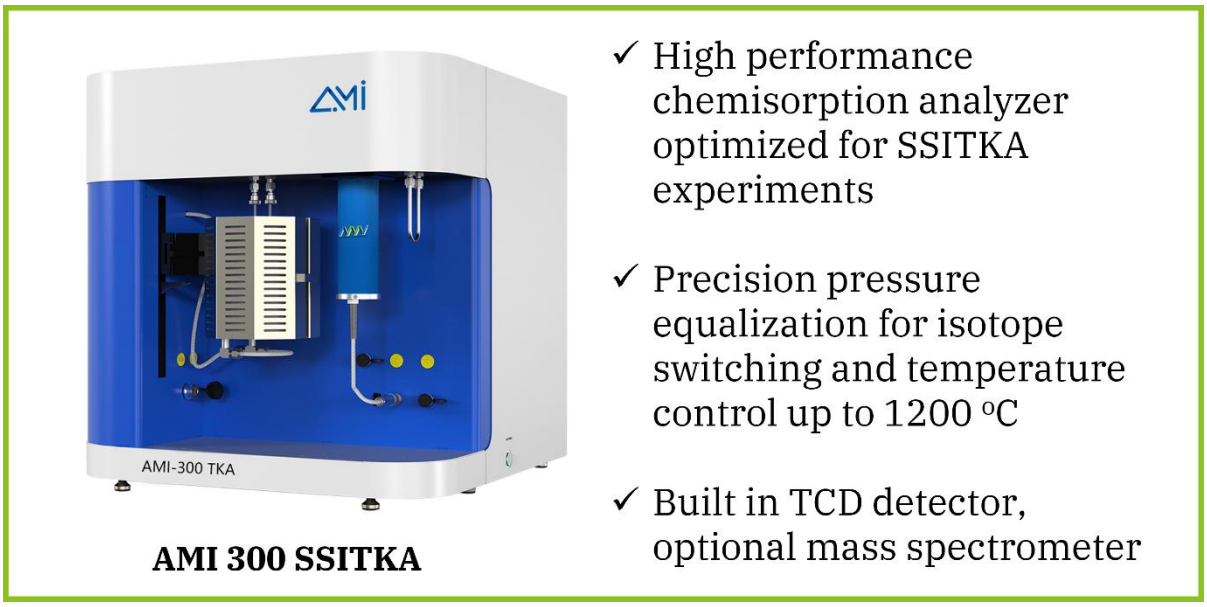

*Figure 5: Highlighted features of **AMI 300 SSITKA** chemisorption analyzer*

6. References

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