

## Steady-State Isotopic Transient Kinetic Analysis (SSITKA) in Practice

Building on our previous overviews of SSITKA, this article delves into the core principles and computational methods behind the technique. In addition, it explores how SSITKA can be integrated with in-situ infrared spectroscopy to provide deeper insight into surface reactions and active site behavior.

### 1. Introduction to SSITKA Technology

#### 1.1 SSITKA instrumentation

The schematic diagram of the SSITKA experimental setup is shown in Figure 1a. It consists of three main components: a gas flow control system, a reactor, and a mass spectrometer. The gas flow system must support steady-state transient operation, enabling rapid and stable switching between isotopic feeds. It is also essential that both the pre- and post-switch conditions are well-defined and reproducible. The mass spectrometer must be capable of fast response to accurately capture transient signals.

Most SSITKA experiments today rely on microreactor-based systems that are either manual or semi-automated, often leading to operator-induced variability. The **AMI 300 SSITKA** system, shown in Figure 1b, addresses this challenge by enabling fully integrated SSITKA experiments through dedicated gas circuit design and coupled mass spectrometry, as shown in the software interface in Figure 2. Transient switching is achieved using a four-way valve, which alternates between two feed streams: Aux Gases and Blend Gases. These streams introduce either the unlabeled reactant ( $^{12}\text{CO}$ ) or the isotopically labeled reactant ( $^{13}\text{CO}$ ). Upon valve switching, the system seamlessly transitions from  $^{12}\text{CO}$  to  $^{13}\text{CO}$  under steady-state conditions.

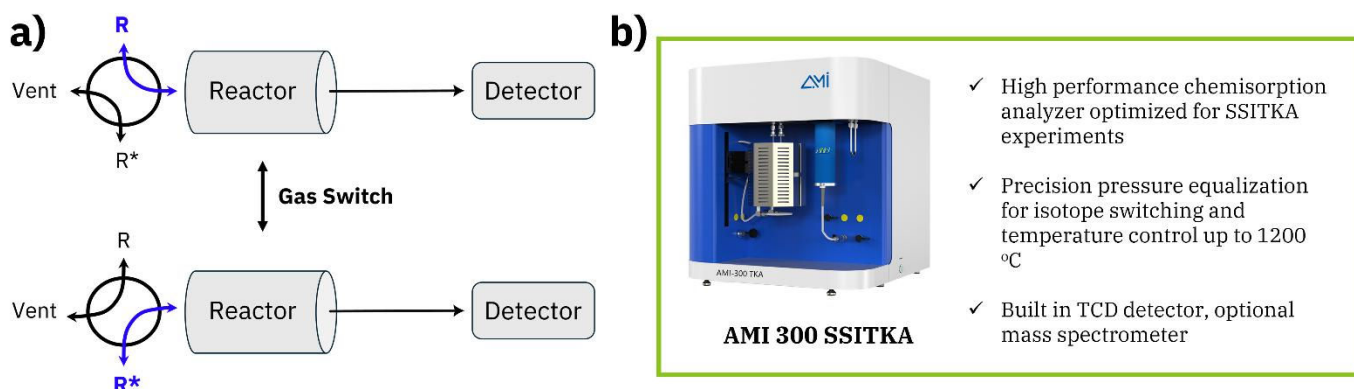


Figure 1: a) Schematic diagram of SSITKA experimental device and b) highlighted features of AMI 300 SSITKA

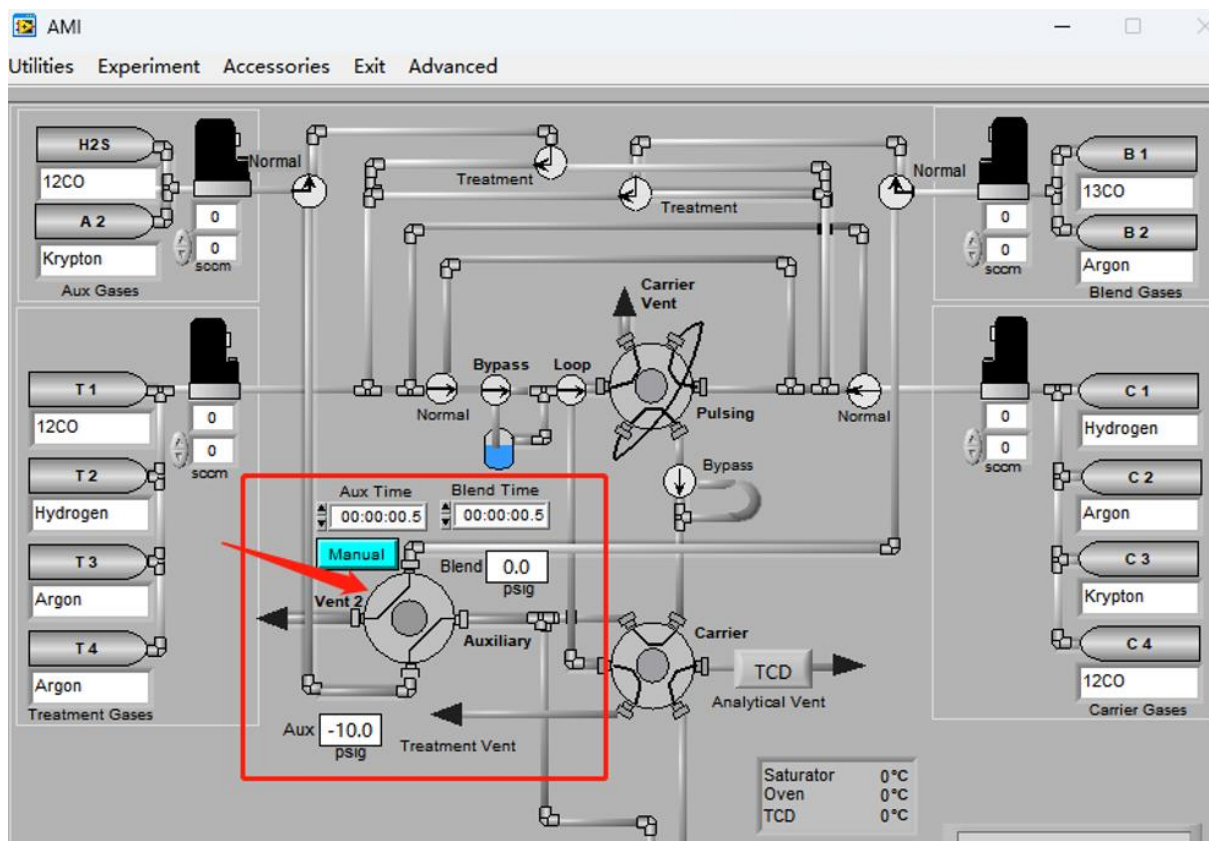


Figure 2: Software interface of **AMI 300 SSITKA**

**AMI 300 SSITKA** experiments can be executed automatically following the program shown in Figure 3. The fully automated process eliminates the need for manual intervention, significantly reducing the risk of human error and improving the accuracy and reproducibility of test results. The procedure is both practical and user-friendly, ensuring reliable operation even for complex transient kinetic studies.

## 1.2 Kinetic parameters

The surface residence time ( $\tau_p$ ) of surface intermediates and the surface coverage ( $N_p$ ) are determined by monitoring signal intensity via mass spectrometry, as illustrated in Figure 4a. Here, P represents the unlabeled product, P\* is the isotopically labeled counterpart, and I denotes an inert tracer. At time  $t = 0$ , the four-way valve switches, introducing the labeled reactant. As a result, P and I display a decay in signal intensity, while P\* shows a corresponding increase. By normalizing the decay profile of P, the transient response curve shown in Figure 4(b) is obtained.

Without making kinetic assumptions or defining surface reaction mechanisms, two key parameters can be directly extracted from the transient response curve: the surface residence time (or surface lifetime)  $\tau_p$  of the intermediate species that form product P, and the surface coverage  $N_p$  of those intermediates. The expression for calculating  $N_p$  is given below:<sup>(1)</sup>

$$N_p = \int_0^{\infty} r_p(t) dt \quad (1)$$

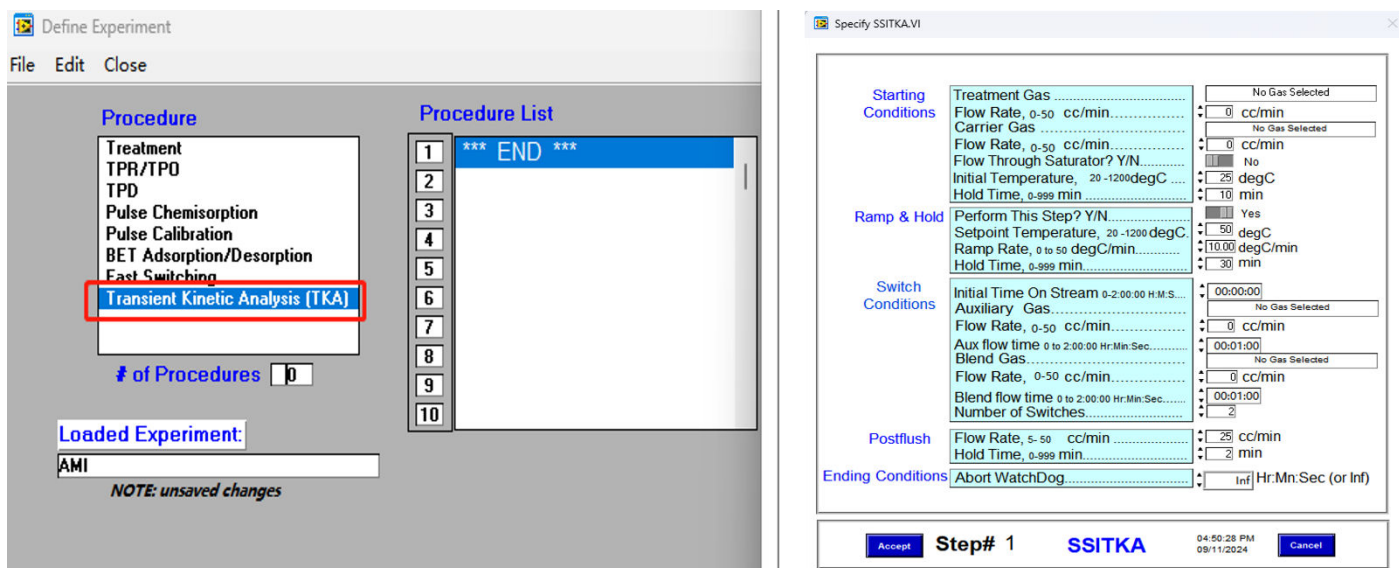


Figure 3: SSITKA program setting and kinetic parameter calculations on AMI-300 SSITKA

During the experiment, the reactants were rapidly switched while maintaining a constant reaction rate. The reaction rate of the unlabeled product was determined using the following equation, where  $r_p(t)$  represents the steady-state reaction rate of the unlabeled product, and  $r_p(t)$  denotes the reaction rate of the isotopically labeled product.<sup>(2)</sup>

$$r_p(t) = r_p - r_{p^*}(t) \quad (2)$$

$r_p(t)$  is the steady-state reaction rate of the unlabeled product, and  $r_p(t)$  is the reaction rate of the isotopically labeled product. As shown in Figure 4(b), normalizing the decay of the unlabeled product yields the transient response curve. The expression for  $F_p(t)$  is given as follows:

$$F_p(t) = \frac{r_p(t)}{r_p} \quad (3)$$

By rearranging and calculating the above three formulas, the surface residence time  $\tau_p$  of the intermediate species can be obtained.

$$\tau_p = \int_0^{\infty} F_p(t) dt = \int_0^{\infty} \frac{r_p(t)}{r_p} dt = \frac{N_p}{r_p} \quad (4)$$

Integrating the transient response curve yields the surface residence time  $\tau_p$ , as shown in Figure 5.

The surface coverage ( $\theta$ ) of intermediates, the reaction rate constant ( $k$ ), and the turnover frequency (TOF) are calculated using chemisorption techniques to determine the total number of exposed metal atoms ( $N_a$ ) on the catalyst surface.

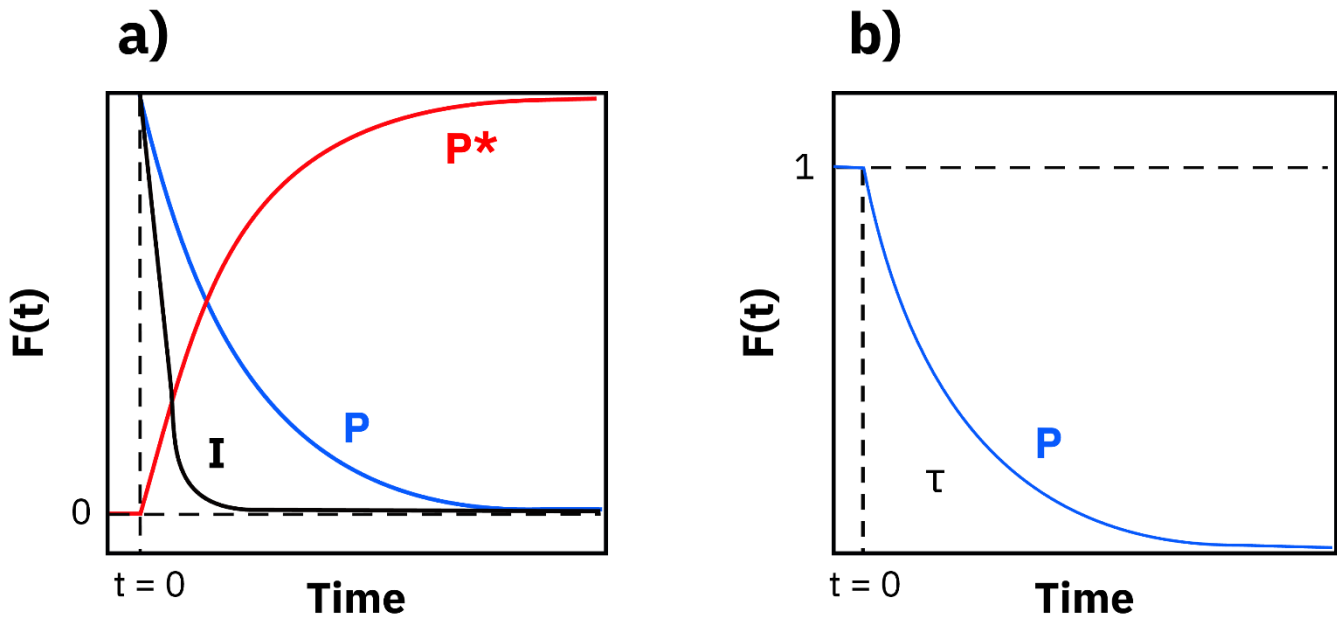


Figure 4: a) Mass spectrum of unlabeled product (P), labeled product (P\*), and inert tracer (I); b) corresponding transient response curve

$$\theta = \frac{N_p}{N_c} \quad (5)$$

Assuming that the chemical reaction on the surface is pseudo-first-order, the rate equation of the pseudo-first-order reaction can be expressed as:

$$r_p = kN_p \quad (6)$$

Thus, the pseudo-first-order reaction rate constant is obtained:

$$K = \frac{r_p}{N_p} = \frac{1}{\tau_p} \quad (7)$$

TOF (turnover frequency) represents the number of catalytic reactions occurring per unit time per active site. It reflects the catalyst's instantaneous efficiency based on the number of surface active sites. The formula is as follows:

$$TOF = \frac{r_p}{N_p} \times \theta = \frac{1}{\tau_p} \times \theta = K \times \theta \quad (8)$$

Here,  $\theta$  represents the surface coverage of intermediate species. The number and distribution of active sites on the catalyst surface can be analyzed using deconvolution techniques, enabling further investigation into the kinetics and mechanism of the catalytic reaction.

### 1.3 Modeling of SSITKA

A heterogeneous catalytic reaction often proceeds through one or more surface-bound intermediate steps. The general parameters introduced earlier— $\tau_p$  (the total surface residence time of intermediate species) and  $N_p$  (the total quantity of surface intermediates leading to product P)—represent the overall behavior of all intermediates involved in forming product P. To distinguish the contribution of individual intermediates, Shannon<sup>(3)</sup> and Chen et al.,<sup>(4)</sup> building on the work of Biloen et al.,<sup>(5)</sup> proposed a surface reaction mechanism model. This model categorizes reactions into reversible and irreversible types, and further into cases involving single, sequential (series), parallel, or more complex arrangements of intermediate species. Based on these classifications, transient response models were derived using material balance principles. These models allow for the extraction of dynamic parameters such as the quantity and residence time of each intermediate species involved in producing product P.

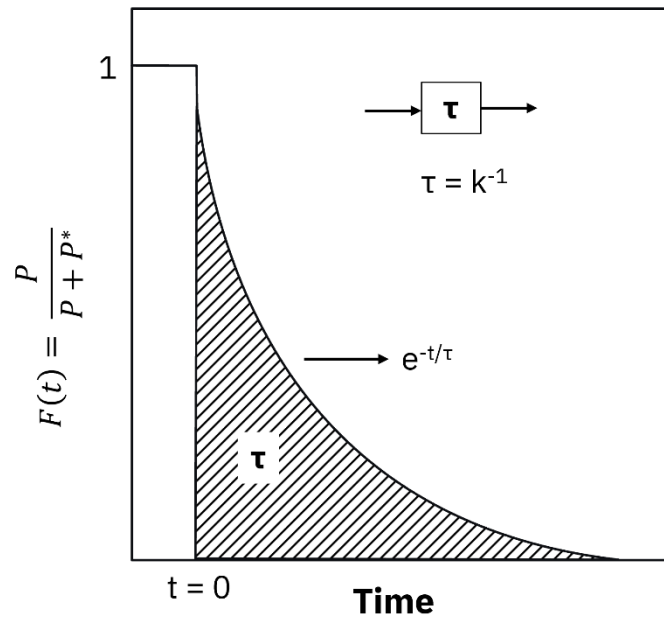


Figure 5: Surface residence time,  $\tau$

## 2. Factors Influencing SSITKA Experiments

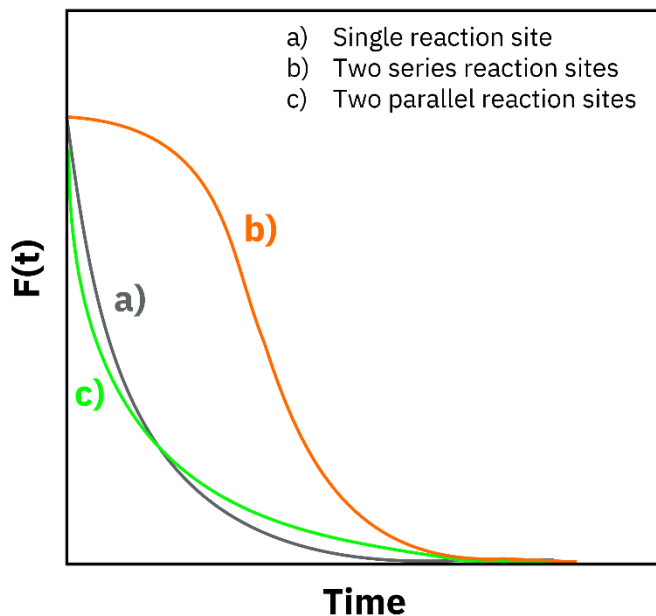


Figure 6: Schematic diagram of transient responses for different surface reaction mechanisms

### 2.1 Inferring catalyst surface reaction mechanisms

Kobayashi et al.<sup>(6)</sup> demonstrated experimentally that the shape of the transient response curve can provide insights into the underlying reaction mechanism. Building on this, Shannon et al. presented representative response profiles for different irreversible reaction pathways—specifically, cases involving a single intermediate, two intermediates in series, and two intermediates in parallel—as illustrated in Figure 6.

As shown in Figure 6, the transient response curves exhibit characteristic S-shaped profiles. Curve 6b, which shows the slowest decay, corresponds to two sequential (serial) reaction intermediates—reflecting the extended time

required for consecutive reactions at two sites. Curve 6a, displaying a single exponential decay, represents a single intermediate species. Curve 6c, with a multi-exponential decay pattern, corresponds to two parallel reaction intermediates, where the simultaneous operation of different reaction pathways leads to faster, overlapping decay components. By analyzing these distinct curve shapes, researchers can readily differentiate between kinetic models and infer the nature of surface reactions occurring on the catalyst.

## 2.2 Chromatographic effects and re-adsorption

In SSITKA experiments, both reactants and products can adsorb not only on the catalyst surface but also on the reactor walls and connecting pipelines, introducing a chromatographic effect. This effect can distort transient responses but may be minimized by reducing the distance from the four-way valve to the detector, increasing gas flow rates, and thermally insulating the transfer lines. The **AMI 300 SSITKA** system addresses these challenges through the use of 1/16-inch tubing to reduce dead volume, thermal insulation of the valve box, and precise gas flow control via mass flow controllers—measures that collectively enhance measurement accuracy.

Additionally, product re-adsorption can significantly influence transient response data. When re-adsorption occurs at active sites, it reduces catalytic activity and lowers reaction rates. If it occurs at non-reactive sites, the activity remains unaffected, but the measured surface residence time of the product becomes artificially extended—combining the actual intermediate lifetime with the re-adsorption time. To correct for this, inert tracers and empirical correction formulas are commonly applied.

$$\tau_{p,corrected} = \tau_{p,measured} - \tau_{inert} - x\tau_{reactant} \quad (9)$$

Where  $\tau_{inert}$  is the surface residence time during inert gas response,  $x$  is empirically taken as 0.5.

## 2.3 Isotope Effect

SSITKA experiments are typically conducted under the assumption of steady-state conditions, with isotope effects considered negligible—that is, the kinetic behavior of isotopically labeled and unlabeled species is assumed to be identical. However, special attention is required when working with hydrogen and its isotopes (e.g., H/D), as the significant differences in mass and bond energy can lead to pronounced kinetic and thermodynamic effects. During H/D isotope exchange, changes in reaction rates and surface intermediates may disrupt steady-state conditions, potentially compromising experimental reliability. As a result, H isotope SSITKA experiments must be approached with caution. Despite these challenges, such experiments are valuable for probing surface reactivity, particularly in identifying bond cleavage events associated with adsorption, desorption, or reaction of specific molecular species.

### 3. SSITKA in Conjunction with Spectroscopy

SSITKA is a powerful technique for determining the abundance and kinetic parameters of surface intermediates. However, its primary limitation is the inability to directly characterize the chemical structure of these intermediates or observe their surface reactions in real time. In contrast, in situ infrared (FTIR) spectroscopy enables direct observation of adsorbed species under reaction conditions.<sup>(7,8)</sup> By integrating SSITKA with FTIR, it becomes possible to accurately identify surface intermediates—including their chemical structure and surface coverage—and to distinguish reactive adsorbed species from non-reactive ones.<sup>(9)</sup> Figure 7 shows the combined chemisorption/infrared spectroscopy system developed by **AMI**, which can combine the SSITKA technique with in situ FTIR spectroscopy for advanced surface characterization.



Figure 7: Highlighted features of **AMI-300 IR** chemisorption analyzer

### 4. Conclusions

Since its development in the 1970s, SSITKA has been widely applied to investigate the mechanisms of numerous important industrial catalytic reactions. Today, the integration of SSITKA with spectroscopic techniques enables direct observation of surface intermediates and provides deeper insight into reaction mechanisms. Furthermore, combining SSITKA with complementary methods such as kinetic modeling and density functional theory (DFT) enhances our understanding of reaction pathways. The **AMI 300 SSITKA** is the only commercially available SSITKA system that also serves as a fully featured chemisorption analyzer, offering unmatched versatility in a single platform. By leveraging the strengths of SSITKA alongside these advanced techniques, researchers can obtain a comprehensive picture of catalytic processes under true reaction conditions, facilitating the elucidation of complex chemical mechanisms.

## 5. References

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