Steady-State Isotopic Transient Kinetic Analysis (SSITKA) Technology in Catalytic Reactions

1. Background

Catalysts are at the heart of modern chemical manufacturing, with more than half of all chemical products depending on catalytic processes. Improving catalyst performance requires a deeper understanding of the physicochemical phenomena that occur at the catalyst–reactant interface, including diffusion, adsorption/desorption, surface reactions, and structural changes at the surface.[1] To investigate these processes, researchers study both the reaction mechanism and key kinetic parameters, such as surface coverage and reaction rates. One particularly powerful technique is SSITKA (steady-state isotopic transient kinetic analysis), first introduced in the 1970s by Happel,[2,3] Bennett,[4] and Biloen.[5]

SSITKA enables the measurement of kinetic parameters under true steady-state conditions. By rapidly switching from a reactant gas to its isotopically labeled analog—while maintaining constant flow, pressure, temperature, and catalyst surface state—SSITKA captures real-time information on surface intermediates, site coverages, and turnover rates without disrupting the reaction equilibrium. This application note reviews key literature examples of SSITKA in catalysis and highlights why **AMI** developed the **AMI 200** and then the **300 SSITKA**—a fully integrated system designed to meet the growing demand for reliable, precise kinetic measurements.

1.1 Definition of SSITKA

SSITKA is a technique that rapidly switches from a reactant gas to its isotopically labeled counterpart under steady-state conditions. Using mass spectrometry, the system monitors transient response curves as unlabeled reactants and products decrease and labeled species increase. This enables the quantitative study of heterogeneous catalytic mechanisms and surface kinetics. The “steady state” ensures constant flow rate, pressure, temperature, surface coverage, and reactant/product concentrations throughout the switch—minimizing interference from isotopic effects. Since most industrial catalytic processes operate under steady-state conditions, SSITKA provides highly relevant insights into reaction pathways, site coverages, and apparent activation energies. While early versions relied on radioactive isotopes, modern SSITKA systems now use stable isotopes such as ^{13}C, ^{18}O, ^{15}N, and D_2. The isotopic switch is typically achieved with a fast-acting four-way valve, alternating between labeled and unlabeled feeds. Analysis of the resulting transients reveals key kinetic parameters and mechanistic details.

2. SSITKA in Catalytic Mechanism Studies

SSITKA enables direct measurement of key kinetic parameters, including mean residence time, surface intermediate concentrations, and intrinsic rate constants. These values provide quantitative insight into active site density, reaction pathways, and the influence of supports, promoters, alloying, and deactivation mechanisms.

2.1 SSITKA in ethylene oxidation

Ethylene, a key building block in organic synthesis, can be selectively oxidized to either acetaldehyde (using PdCl/CuCl catalysts) or ethylene oxide over silver-based catalysts. Despite decades of study, the identity of the active oxygen species (e.g., Ag_x–O vs. Ag–O–O–Ag) and the dominant reaction mechanism—whether Langmuir–Hinshelwood (L-H), Eley–Rideal (E-R), or Mars–van Krevelen (MvK)—remains under debate. To address this, Professor Israel E. Wachs and his team at Lehigh University combined in situ Raman spectroscopy with SSITKA (using the **AMI 200**) to investigate ethylene oxidation over Ag/α-Al_2O_3 catalysts and clarify both the nature of the active sites and the operating mechanism.(6)

Mass spectra from SSITKA experiments showed that after switching from $^{16}O_2 \rightarrow {}^{18}O_2$, ethylene oxide and CO_2 signals rapidly decay to zero within ~7 minutes, confirming ethylene epoxidation followed the L-H mechanism (requiring adsorbed ethylene and Ag_4-O_2 species). Post-switch, $C_2H_4{}^{16}O$ and $C^{16}O_2$ signals gradually decreased, while $C^{16}O^{18}O$ rose, indicating MvK (lattice oxygen) participation in CO_2 formation. SSITKA demonstrated that ethylene epoxidation predominantly followed L-H, while complete oxidation involved both L-H and MvK mechanisms.

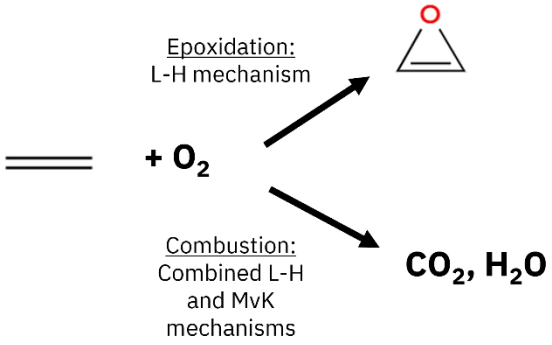

Figure 1: Reaction scheme for ethylene oxidation over Ag/α-Al_2O_3 catalyst showing the proposed epoxidation and combustion mechanisms [paraphrased from (6)]

2.2 SSITKA in Fischer-Tropsch (FT) synthesis

The conversion of synthesis gas (CO + H_2) into clean fuels and value-added chemicals is a key pathway for the efficient utilization of coal. However, the complexity of the product distribution and low selectivity of the reaction pose challenges to its industrial application. In recent years, cobalt-based catalysts have gained attention for producing high-quality diesel fuels, owing to their relatively slow deactivation and favorable carbon chain growth characteristics. While catalyst additives are known to significantly influence performance, their effects on reaction kinetics remain underexplored. To address this, Professor Yang Jia's team at the Norwegian University of Science and Technology, in collaboration with Professor Xiaoli Yang's group at Qingdao University, modified Co-based catalysts with promoters Rh, Ir, Sb, and Ga to evaluate their effects on Fischer–Tropsch synthesis.(7) SSITKA was used to investigate the catalysts' intrinsic activity and surface adsorption behavior, providing deeper insight into the role of these additives in reaction kinetics.

Catalyst	N_{CO} (µmol/g cat.)	N_{CHx} (µmol/g cat.)
Co/Al_2O_3	110	8
$CoRh/Al_2O_3$	234	16
$CoIr/Al_2O_3$	236	13
$CoSb/Al_2O_3$	53	4
$CoGa/Al_2O_3$	39	1

Table 1: Intermediate CO and CH_x surface concentrations during Fischer-Tropsch reaction calculated using the SSITKA technique [summarized from (7)]

SSITKA experiments involved switching from $^{12}CO/H_2/Ar$ to $^{13}CO/H_2/Ar$. Normalized transient curves were analyzed to derive SSITKA parameters, which are summarized in Table 1. Through SSITKA parameter analysis, it was found that: The amount of N_{CO} surface intermediates of the reactants on $CoRh/Al_2O_3$

and CoIr/Al_2O_3 was 234 and 236 μmol/g cat., respectively, which was twice that of unpromoted Co/Al_2O_3 (110 μmol/g cat.). The amount of N_{CO} on CoSb/Al_2O_3 and CoGa/Al_2O_3 catalysts was 53 and 39 μmol/g cat., respectively. The data indicates that precious metals Ir and Rh promoted the catalyst and increased more active sites, so that more CO could be adsorbed. The quantity of surface intermediates of the product N_{CHx} showed the same trend. However, non-precious metal Sb and Ga showed the opposite trend. At the same time, the residence time of the four promoters was analyzed, and it was found that the residence time of the four promoters had little difference. The precious metals had no obvious effect on the intrinsic activity of the catalyst, while the non-precious metals reduced the active site and the intrinsic active site.

The reaction rate of CO was found to be independent of N_{CO} concentration, suggesting that CO conversion is not directly governed by N_{CO} coverage. A linear relationship with N_{CHx} concentration was observed, indicating that CH_x intermediates play a key role in determining the reaction rate of CO. These additives influence the surface concentration of CH_x species during the reaction, which in turn affects both the CO reaction rate and the carbon chain growth rate constant, ultimately altering the product distribution. Further analysis suggests that these effects stem from electronic modifications introduced by the additives. Changes in the electronic properties of the active metal led to reduced adsorption strength, thereby shifting surface reactivity and selectivity.

In summary, this paper by Yang J. et al. provides kinetic insight into how different additives influence the performance of Co-based catalysts in Fischer–Tropsch synthesis. The SSITKA technique explored the intrinsic activity and surface adsorption properties. It revealed that promotors changed the value for N_{CHx}, which governed catalytic activity. Higher quantities of CH_x intermediates on the surface present on CoIr/Al_2O_3 and CoRh/Al_2O_3 led to an improved CO conversion rate over the transition metal promoted Co catalysts and the unpromoted Co catalyst. Their work identifies the key kinetic factors underlying enhanced catalytic activity and offers a foundation for further catalyst optimization.

3. Conclusions

Steady-state isotopic transient kinetic analysis (SSITKA) is a powerful technique for quantifying surface intermediates and extracting kinetic parameters under true reaction conditions. With advancements in instrumentation and analytical methods, SSITKA is increasingly combined with complementary approaches such as in situ spectroscopy, kinetic modeling, and DFT calculations to provide a more comprehensive understanding of catalytic mechanisms. Recognizing the growing need for integrated, precise, and user-friendly tools, the **AMI 300 SSITKA** system—a dedicated platform designed to perform reliable SSITKA experiments with high temporal resolution, stable gas switching, and seamless coupling to mass spectrometry. In

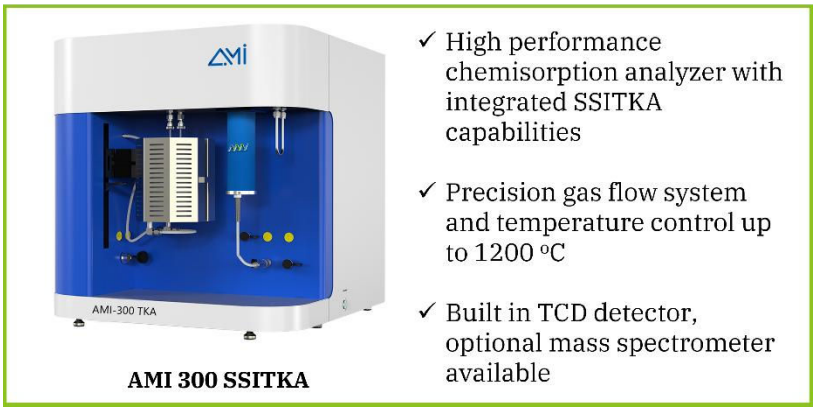

*Figure 2: Highlighted features of **AMI 300 SSITKA***

future articles, we will explore the underlying principles of SSITKA and demonstrate how the **AMI 300 SSITKA** supports advanced catalyst characterization and kinetic analysis.

4. References

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