

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

Background Introduction

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, Bennett, and Biloen.

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 then 300SSITKA**—a fully integrated system designed to meet the growing demand for reliable, precise kinetic measurements.

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 [2]. 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.

Applications of SSITKA in Catalysis

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.

SSITKA in Catalytic Mechanism Studies

Ethylene, a key building block in organic synthesis, can be selectively oxidized to either acetaldehyde (using PdCl/CuCl catalysts) or ethylene oxide (EO) over silver-based catalysts. Despite decades of study, the identity of the active oxygen species (e.g., $\text{Ag}_x\text{-O}$ 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 to investigate ethylene oxidation over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts and clarify both the nature of the active sites and the operating mechanism [3].

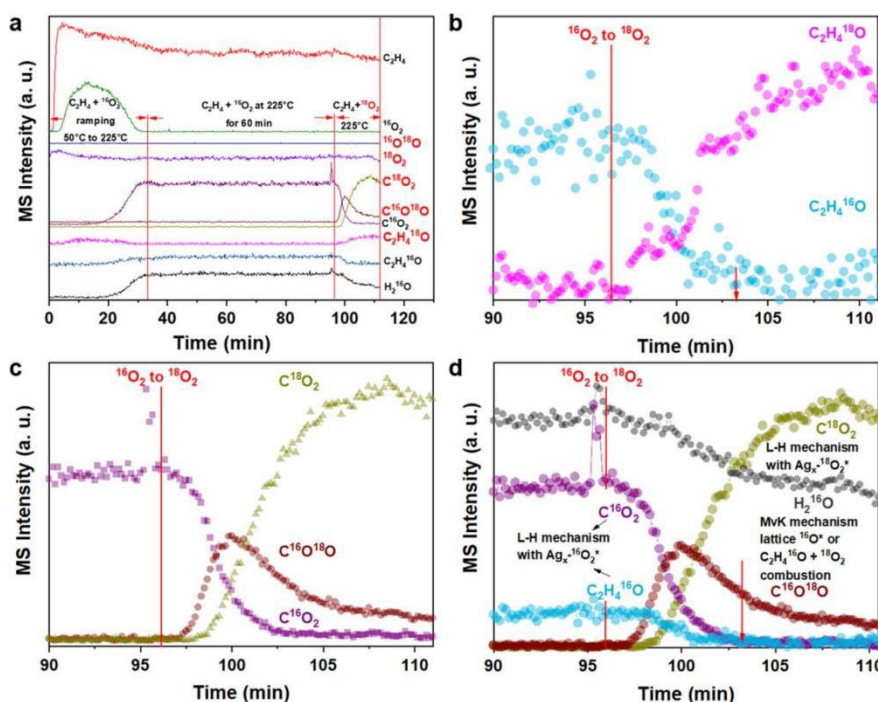


Figure 1: SSITKA Experiment for $\text{C}_2\text{H}_4 + {}^{16}\text{O}_2 \rightarrow {}^{18}\text{O}_2$

Figure 1 shows mass spectra from SSITKA experiments using **AMI-200**. After switching from $C_2= + ^{16}O_2 \rightarrow ^{18}O_2$ (Figure 1b, c), EO and CO_2 signals rapidly decay to zero within ~ 7 minutes, confirming ethylene epoxidation follows 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 decrease, while $C^{16}O^{18}O$ rises, indicating MvK (lattice oxygen) participation in CO_2 formation. SSITKA demonstrates that ethylene epoxidation predominantly follows L-H, while complete oxidation involves both L-H and MvK mechanisms.

SSITKA in Fischer-Tropsch (F-T) 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 Rh, Ir, Sb, and Ga to evaluate their effects on Fischer-Tropsch synthesis [4]. 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.

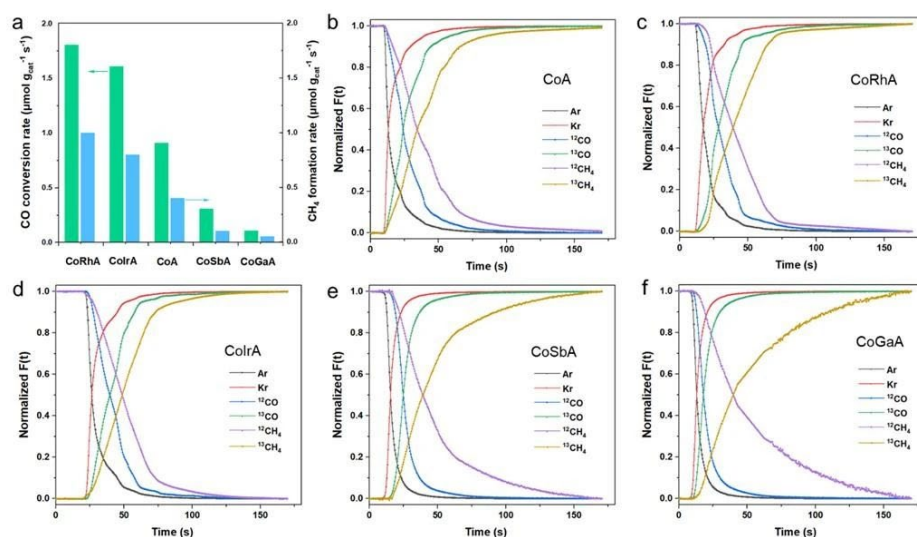


Figure 2: (a) CO conversion rate and CH_4 formation rate on CoM/ Al_2O_3 catalyst under SSITKA condition. Normalized transient curves of (b) CoA, (c) CoRhA, (d) CoIrA, (e) CoSbA, and (f) CoGaA.

SSITKA experiments involved switching from $^{12}\text{CO}/\text{H}_2/\text{Ar}$ to $^{13}\text{CO}/\text{H}_2/\text{Ar}$. Normalized transient curves (Figure 2) were analyzed to derive parameters in Table 1:

Table 1: SSITKA Parameters for Co-Based

	CoA	CoIrA	CoRhA	CoSbA	CoGaA
R_{CO} [$\mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$]	0.90	1.60	1.80	0.30	0.10
R_{CH_4} [$\mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$]	0.40	0.80	1.00	0.10	0.05
τ_{CO} [s]	10.7	11.4	11.4	10.1	5.8
N_{CO} [$\mu\text{mol g}_{\text{cat}}^{-1}$]	109.6	236.4	233.7	53.3	31.9
τ_{CH_4} [s]	17.7	17.5	16.1	26.0	35.0
N_{CH_x} [$\mu\text{mol g}_{\text{cat}}^{-1}$]	7.8	13.3	15.9	3.6	1.1
k_{CH_x} [s^{-1}]	0.056	0.057	0.062	0.038	0.029
k_{g^*} [s^{-1}]	0.037	0.031	0.026	0.061	0.143

Through steady-state SSITKA parameter analysis, it is found that: The amount of N_{CO} surface intermediates of the reactants of CoRh/ Al_2O_3 and CoIr/ Al_2O_3 was (236 and 234 $\mu\text{mol g}_{\text{cat}}^{-1}$), respectively, which was 2 times higher than that of CoA (109.6 $\mu\text{mol g}_{\text{cat}}^{-1}$). The reduction of CoSb/ Al_2O_3 and CoGa/ Al_2O_3 catalysts is 53 and 39 $\mu\text{mol g}_{\text{cat}}^{-1}$, respectively. These data indicate that the precious metals Ir and Rh can promote the catalyst and increase more active sites, so that more CO can be adsorbed. The quantity of intermediates on the surface of the product N_{CH_x} has the same trend. However, non-precious metal Sb and Ga auxiliaries showed the opposite trend. At the same time, the residence time of the four auxiliaries was analyzed, and it was found that the residence time of the four auxiliaries had little difference, and the precious metal had no obvious effect on the intrinsic activity of the catalyst, while the non-precious metal reduced the active site and the intrinsic active site.

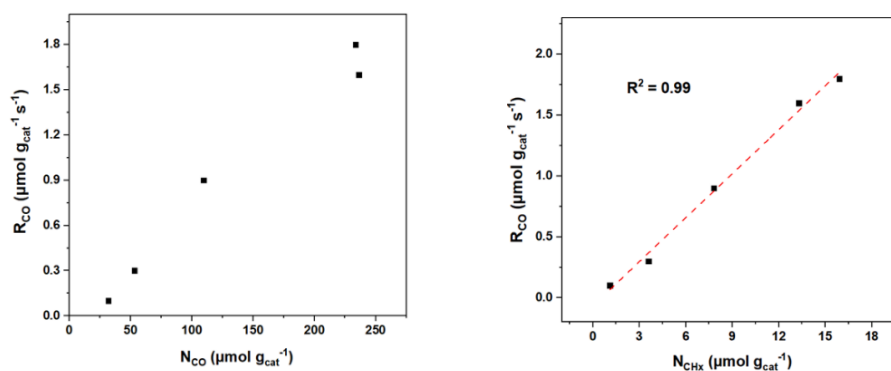


Figure 3: Relation between CO reaction rate of CoM/ Al_2O_3 and concentration of CO and CHx intermediates

References

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