

MINI REVIEW

Experimental methods in chemical engineering: Temperature-programmed oxidation—TPO

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Abstract

Temperature-programmed oxidation (TPO) probes the oxidative capacity and redox properties of solid materials—catalysts, metal oxides, perovskites, and carbonaceous deposits. It identifies coke type, distribution, and reactivity. TPO instruments pass an oxidizing gas (diluted O₂, air, or less commonly N₂O, CO₂, or CO) through a micro-reactor loaded with 20 mg to several 100 mg of solids, housed in a furnace. As the furnace ramps temperature up ($\geq 900^\circ\text{C}$), a thermal conductivity detector, mass spectrometer, or infrared detector monitors effluent O₂ concentration. Operating conditions determine peak position, shape, and intensity-input parameters to derive O₂ consumption, kinetics, and surface reactivity: Increasing the heating rate shifts oxidation peaks to higher temperatures, whereas increasing the O₂ concentration accelerates oxidation and shifts peaks to lower temperatures. Changing sample mass and gas flow modify signal resolution; kinetics rather than mass transfer govern reaction rates with less than 100 mg for slow reactions and small particles. TCDs are adequate to characterize simple metal oxide chemistry ($\text{M} + \delta\text{O}_2 \rightarrow \text{MO}_{2\delta}$). For complex oxides, perovskites, and coked catalyst, complementary analytical techniques like X-ray diffraction, Raman spectroscopy, and mass spectrometry improve TPO's capability to identify phase changes, reaction kinetics, and mechanisms. Standard deviation on repeat runs approach 1%. In 2025, articles in journals Web of Science assigns to physical chemistry mention TPO most, followed by chemical engineering, energy & fuels, then multi-disciplinary chemistry. A bibliometric analysis assigned keywords into four categories: catalyst, Ni, CH₄, H₂; oxidation, mechanism, TiO₂; oxide, reduction, nanoparticle, CO; and, NOX, selective catalytic reduction, Cu.

KEYWORDS

catalyst, coke, oxide, reduction, TCD, temperature-programmed oxidation, TPO

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1 | INTRODUCTION

Adsorption is a fundamental surface phenomenon in material science. Many chemical processes, from gas separation and pollutant capture to heterogeneous catalysis and energy storage, are governed by the interaction between an adsorbent surface and adsorbate (adsorbed molecule). Designing efficient processes and suitable materials requires insight into the adsorbent–adsorbate interaction's strength, nature, and reversibility.^[1]

Physisorption (physical adsorption) is a reversible process in which adsorbate molecules weakly bond to the adsorbent surface via van der Waals forces. Adsorbate–adsorbent interactions, such as covalent bonding, electrostatic forces, or charge transfer, which release more heat, are stronger for chemisorbed species. Sorption processes also involve a series of irreversible chemical reactions that form surface complexes. Temperature-programmed methods are chemisorption-based tools to characterize the intrinsic reactivity of materials' surfaces. Treatment conditions and carrier gas divide these techniques into temperature-programmed desorption (TPD), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and temperature-programmed surface reaction (TPSR).

TPO explores the oxidative reactivity of surface species, such as carbonaceous deposits, reduced metals, or defective oxides. The temperature of the material is increased slowly at a constant heating rate under a dilute oxidizing gas stream. Oxygen consumption and the evolution CO and CO₂ disclose the type and distribution of reactive sites, the reaction mechanism, and the ease of regeneration or oxidation.^[2,3] It also identifies coke types, quantifies coke deposition, and evaluates the regeneration and deactivation mechanisms.^[1]

Compared to thermogravimetric analysis (TGA), which is based on the sample mass change, TPO, based on oxygen consumption, provides more reliable kinetic data: oxygen that chemisorbs modifies how the mass changes, which distorts how to interpret the kinetics.^[4] Moreover, the flow dynamics in a TGA crucible are non-ideal, which confounds oxygen diffusion and reaction kinetics.^[5] In flow-through TPO configurations, the gas phase approaches plug-flow, which facilitates interpreting the O₂ signal. TPO is more comprehensive than TGA, as it simultaneously characterizes and quantifies of carbonaceous species, eliminating post-processing.^[6] TPO also identifies changes in coke morphology, while TGA fails to capture this phenomenon.^[7] Raman spectroscopy directly identify carbonaceous structures and degrees of ordering; coupled with TPO, it distinguishes between amorphous and highly disordered

carbon from ordered carbon and graphitic structures, even for samples with very low carbon content.^[8]

TPO assesses the oxidation and redox properties of metals and metal oxides, defective oxides, soot, biochar, coal, graphene, nanostructured carbons, or any other carbon material.^[9,10] It characterizes metal–oxygen vacancies, lattice mobility, and surface reactivity of metal oxides. It is also an effective technique for evaluating the oxidation resistance and structural order of carbon-based materials such as graphene and carbon nanotubes. This tutorial review highlights how TPO connects fundamental surface chemistry with applied chemical engineering. The apparent oxidation kinetics depend on controlling the operating conditions precisely—temperature (ramp), pressure, pressure drop, and type of detector.

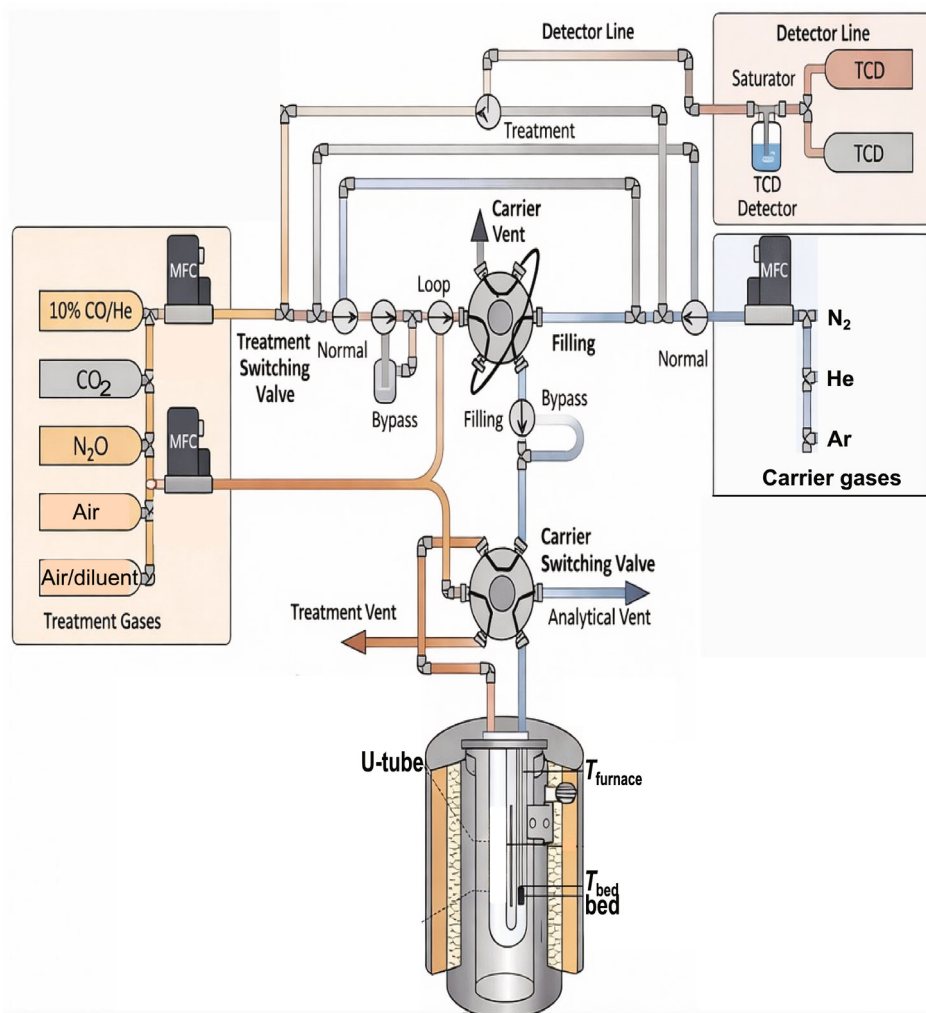
This work is part of a series of over 50 articles dedicated to experimental methods in chemical engineering. The first topic was TPR and it was only 4 pages, while the longest—atomic force microscopy—was 29 pages.^[11] (The CJCE recently accepted an article on cyclic voltammetry that is 51 pages long.)^[12] Together with more detail on the theory section and sources of error, the applications section has expanded. Here, we applied a systematic experimental protocol using a pre-reduced nickel-containing catalyst to identify how heating rate, gas flow rate, sample mass, and probe gas composition affect the TPO profile. The results provide practical guidelines for improving sensitivity, resolution, and repeatability in TPO measurements.

2 | THEORY

2.1 | Instrumentation

TPO is a thermoanalytical technique to study how solid materials oxidize during a controlled temperature ramp. An oxygen containing gas (air, O₂ diluted in He or Ar, CO₂, N₂O, CO, or other oxidant) passes through a powder sample in a microreactor of which a quartz U-tube is a common configuration (Figure 1).^[13,14] A furnace heats the sample while a thermocouple touching the top of the powder bed records the temperature. Thermal conductivity detectors (TCD),^[15] mass spectrometers (MS), and infrared (IR) detectors monitor the effluent stream, thus generating the TPO profile from which we derive oxygen consumption and the evolution of oxidation products. TCDs are easier to calibrate and operate compared to MS but they are non-selective and their sensitivity is poorer. MS identifies species based on their *m/z* signal but overlapping signals confound the analyses, like for CO and N₂. For this reason we substitute Ar for N₂ as a carrier gas.

FIGURE 1 Temperature-programmed oxidation schematic. Typically gas flows from the top down through the bed to maintain fixed bed–plug flow operation. In the case of highly exothermic or endothermic reactions ($\Delta H_{\text{rxn}} > |40 \text{ kJ mol}^{-1}|$) axial and radial temperature gradients develop. Furthermore, gases flow preferentially in the wall region where the voidage is highest. Diluting the solids with inert and minimizing the particle size mitigates these non-uniformities. Alternatively, changing the flow direction so that the U-tube operates as a fluidized bed will minimize both by-passing at the wall and radial and axial thermal gradients, without having to dilute with an inert, while maintaining quasi-plug flow characteristics.^[16,17] Image adapted from Altamira.^[18]



By measuring the signals and recording the rates of oxygen uptake (depleted oxygen) and/or the evolved gases (H_2O , CO , CO_2) as a function of temperature or time, we deduce the oxidation kinetics at the solid surface. For coke-catalyst samples, TPO measures the reactivity and amounts of various carbonaceous species, while for reduced catalysts, it provides the capacity and kinetics of metal re-oxidation. The shape, position, and area of the peaks correlate with the type and quantity of oxidized species (Figure 2). Modern high-sensitivity setups consist of microreactors with less dead volumes, mass flow controllers (MFC) to precisely deliver the carrier and reference gases, and integrated gas switching valves and calibrated detection modules to quantify oxidized species and repeatability.

Carrier gas flow rate, the amount and particle size of the powder, and heating rate all modify the TPO profile. The typical sample load ranges from 10 to a 200 mg to minimize heat and mass transfer limitations. Early studies operated with as much as 500 mg to compensate for the lower sensitivity of the detectors.^[20] An appropriate

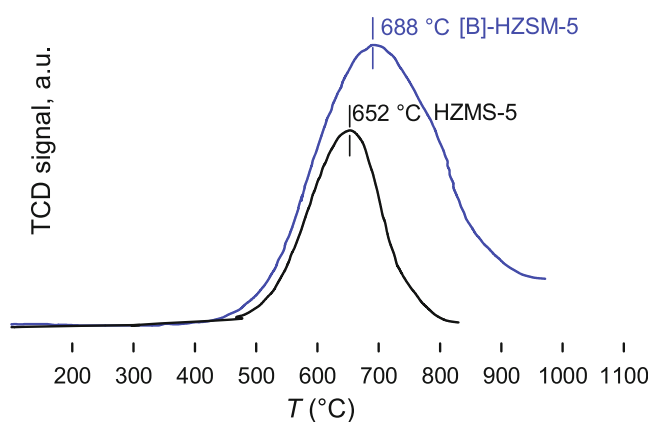


FIGURE 2 Temperature-programmed oxidation profile for a spent methanol-to-olefins boron modified ZSM-5 nanocatalyst after 475 and 1800 h time-on-stream.^[19] The peak area for the [B]-HZSM-5 nanocatalyst (O_2 consumption: 6.58 mmol g^{-1}) is higher than the HZSM-5 nanocatalyst (O_2 consumption: 2.80 mmol g^{-1}). Therefore, the [B]-HZSM-5 nanocatalyst is coked more. Lower temperature removes coke more readily from the HZSM-5 nanocatalyst.

flow rate of carrier gas lies from 30 to 150 mL min⁻¹ and a heating rate of 5–20 °C min⁻¹.

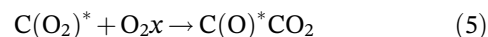
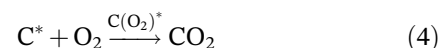
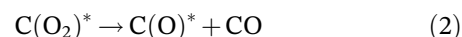
The TPO signal varies with carrier flow rate, gas composition, and temperature programme.^[21] Each of these three parameters must be calibrated to minimize systematic errors. To calibrate the O₂ signal, various volumes of gas dose the sample with either a syringe or a gas loop installed in the TPO instrument. The peak area from the signal is directly related to the amount of O₂ injected to the peak area from the signal. Reference solids with a known stoichiometry, like cupric oxide, also serve as calibration standard: H₂ reduces the sample, then O₂ converts the metal to its oxide (Cu to CuO) while the detector records its O₂ concentration with time. The calibration curve is based on tests with various amounts of Cu in the reactor. To check if the Cu is fully reduced and fully oxidized requires additional analytical tests with XRD, for example.

2.2 | Coke

2.2.1 | Oxidation kinetics

The majority of TPO studies have focused on coke-containing spent catalysts. TPO relies on a heterogeneous reaction between the solid surface and gaseous molecular oxygen.^[22] Carbon oxidation rates increase with increasing temperature. Metal species and inorganic impurities catalyse the oxidation rates at lower temperature.^[23,24] Catalyzed carbon gasification proceeds through three stages: In the first stage, the amount of surface oxide species exceeds the carbon gasified; in the second stage, the carbon gasifies rapidly; and in the third stage the gasification rate reaches steady-state. CO and CO₂ are the primary products of carbon gasification through the decomposition of carbon surface oxides. The CO/CO₂ ratio increases exponentially with temperature and depends on the active surface area available for reaction and the presence of carbon–oxygen surface complexes.^[22]

Li and Brown proposed that carbon oxidation proceeds through a five-step combustion mechanism.^[25] This mechanism follows a single-site scheme involving a free carbon site on the surface (C*) and two oxygenated intermediates: C(O₂)*, which corresponds to an undissociated adsorbed oxygen molecule (Equation (1)), and C(O)*, which corresponds to adsorbed atomic oxygen. CO forms through unimolecular decomposition of oxygenated species (Equations (2) and (3)), whereas CO₂ forms through bimolecular reactions between adsorbed species and oxygen molecules^[25]:



The bimolecular oxidation routes (Equations (4) and (5)) explain the dependence of CO₂ formation on oxygen availability (oxygen partial pressure) and pore transport limitations. Consequently, depending on the TPO conditions, the CO₂ profile exhibit multiple maxima or shoulders. Higher oxygen concentrations in the carrier gas accelerate oxidation kinetics and shift the peaks toward lower temperatures. In contrast, materials with smaller pores, such as micro- and mesoporous structures, retard, broaden, or split the CO₂ peak due to mass transfer limitations. An Arrhenius kinetic model fitted to data on CO₂ formation varies with an order of 0.8–0.9 with respect to oxygen, whereas for CO formation the order lies between 0 and 0.5.^[25,26] Both observations are consistent with unimolecular and bimolecular oxidation mechanisms for CO and CO₂, respectively, and CO formation depends less on oxygen diffusion. Moreover, the formation of stable C(O)* surface complexes retards further oxidation, generating multiple or broadened CO₂ peaks.

Increasing the heating rate shifts all peaks to higher temperatures and improves the resolution of CO and CO₂ profiles.^[25,26] Researchers apply Gaussian or Lorentzian functions to deconvolute multiple overlapping desorption/oxidation peaks associated with surface species, carbon types, or structural domains (Figure 3).^[4,24,27–29]

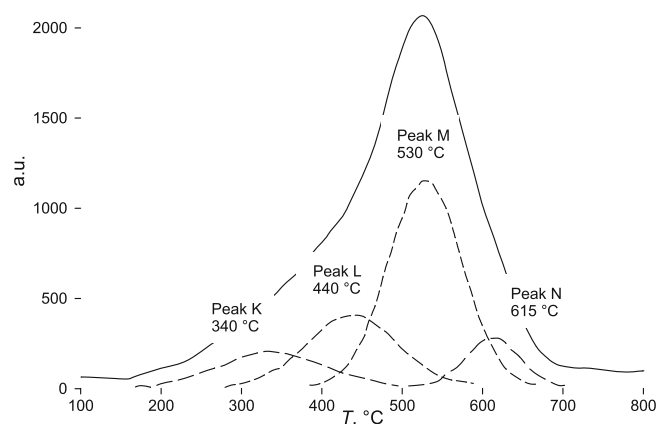


FIGURE 3 Temperature-programmed oxidation spectrum for a coked fluid catalytic cracking catalyst: Overlay composite curve (top); four peaks fitting by Gaussian-type functions (bottom). Reprinted from Bayraktar and Kugler, copyright Elsevier, 2020.^[27]

In the case of fluid catalytic cracking catalysts (FCC) they were: cat-to-oil coke, a low temperature peak related to hydrocarbons desorbing from the coke (peak K); contaminant coke, located on or adjacent to metal contaminants (peak L); conversion coke, formed by acid-catalysed reactions (peak M); and graphitic coke, related to nature of feedstock and catalyst activity (peak N). Some aged catalysts only have the first 3 peaks in TPO analysis.

TPO characterizes different types of carbonaceous deposits and carbonaceous materials.^[7,30] The oxidation temperature correlates with the structural ordering of carbon atoms. Amorphous carbon readily oxidizes due to its lower structural order.^[31] The activation energy for oxidation of these carbons is on the order of 120 to 150 kJ mol⁻¹, while that for highly ordered polyaromatic or graphitic carbon is higher (200 to 270 kJ mol⁻¹); therefore, they oxidize at higher temperatures.^[26] Solid carbon reacts with molecular oxygen at specific active sites. For instance, graphite oxidation initiates at prismatic edges of the laminar sheets and at dislocations, defects, and vacancies in the basal plane vacancies.^[24,32,33] Multiple peaks in TPO profiles reflect differences in the chemical composition and structural ordering of carbon deposits. Beyond identifying combustion temperatures, TPO also reveals how coke structure and porosity evolve during oxidation and how the reaction transitions from chemically controlled to diffusion-limited regimes.^[7] Compared to TGA,^[34,35] however, experimental artefacts such as pyrolysis during heating or catalytic effects caused by impurities can complicate interpretation of TPO profiles.^[30]

2.2.2 | Coke characteristics

Coke refers to undefined hydrogen-deficient organic compounds that accumulate on material surfaces, including catalysts, during hydrocarbon conversion operations.^[10] It deactivates catalysts by blocking pores and covering active sites.^[36,37] TPO can provide information on coke content, coke type, and oxidation kinetics, which can help infer catalyst deactivation mechanisms when combined with complementary characterization techniques.^[25,38–40] We adapt regeneration conditions to maximize coke combustion without compromising the catalyst activity.^[41] The four Gaussian-type peaks assigned to different coke species include: a low-temperature peak associated with desorption of hydrocarbons from coke; contaminant coke, located near metal impurities; conversion coke, formed via acid-catalyzed reactions; and graphitic coke, related to feedstock properties and catalyst history.^[27] TPO experiments identify less ordered and

more reactive carbon, such as activated carbon, at the lowest oxidation temperature, to progressively more ordered structures, such as shot coke, sponge coke, needle coke, and graphite that react at progressively higher temperature.^[29]

The evolution of coke from low-temperature soft structures with less condensed species (oligomers of short-chain olefins) to more aromatic structures containing graphitic species severely affects the catalyst deactivation rate. TPO differentiates between these distinct types of coke based on their oxidation temperature.^[42] While soft coke, associated with low-temperature TPO peaks, is typically reversible and contributes minimally to coke deactivation, hard coke, strongly bound to the surface, reacts at higher temperature. The latter is more stable and is responsible for severe, often irreversible catalyst deactivation.^[37,43,44] In addition, the extent of structural ordering in carbonaceous deposits can be inferred from TPO data, as more ordered structures are less reactive than amorphous carbon and therefore oxidize at higher temperatures.^[45]

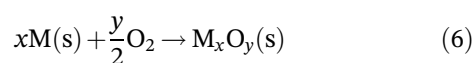
Hard coke mainly forms on acidic supports, whereas soft or amorphous coke forms on metal sites.^[42,46] As a three-dimensional structure, coke exhibits a variable reaction order, ranging from close to 0 to unity as particle size decreases during burn-off. CO and CO₂ are released in the absence of oxygen, suggesting the fact that coke deposits interact with the catalyst support hydroxyl groups, highlighting the role of the catalyst support in coke removal.^[47]

For more complex catalysts containing deposits other than carbon (e.g., sulphur species),^[39,44] we combine TPO with other dynamic analytical techniques, such as TGA, FTIR, and real-time evolved gas analysis. FTIR, for example, tracks CO, CO₂, and SO₂ quantitatively to differentiate oxidation temperature for carbon species from sulphur species.^[48]

2.3 | Metals

2.3.1 | Reduced supported metals

TPO of a reduced metal involves oxygen adsorption, dissociation on the metal surface, and oxide nucleation and growth on the particle:



Oxygen uptake is limited by adsorption and dissociation steps. The temperature at which the oxides react increases with increasing particle size. Consequently, TPO profiles have multiple oxygen peaks since supported

metals contain dispersed sites with different particle sizes. Metal-support interactions also influence peak positions, resulting in several peaks at different temperatures. Increasing the heating rate shifts the peaks to higher temperatures. Increasing the oxygen concentration sharpens the peaks and shifts them to lower temperatures by accelerating oxidation kinetics. For strongly exothermic reactions, highly dispersed metals and smaller metal particles release more heat so the peak emerges at a lower temperature. In this case, a smaller sample mass reduces local rise in the bed temperature; hence, the peak appears in the correct position.^[33,34]

2.3.2 | Metal re-oxidation

Researchers probe the stability and oxidation resistance of metals in catalysts as a function of temperature under oxidative environments and apply TPO to spent catalysts containing both metallic sites (Ni, for example) and coke. Metal oxidation peaks are at lower temperature than coke combustion. Comparing fresh catalysts containing metal particles with spent catalysts containing coke helps assign peaks correctly.^[49]

N₂O-TPO profiles over Ni differ notably from the O₂-TPO profiles because its activation energy is higher: 98 kJ mol⁻¹ compared to 41 kJ mol⁻¹. Oxidation rates are slower and incomplete for N₂O compared to O₂. For this reason, the oxidation state of Ni/Mo catalysts is higher and the selectivity is lower with O₂ compared to N₂O.^[14]

In chemical looping and methane steam reforming, TPO characterizes the reversibility and durability of Ni-based oxygen carriers during cyclic redox operation. The TPO curves for repeated TPR/TPO cycles over Ni/Al₂O₃ up to 950 °C were virtually identical.^[50] These results confirm complete nickel reoxidation and stable metal-support interaction without nickel reaction with alumina. Researchers combined O₂-TPO and CO₂-TPO to study multifunctional chemical looping materials such as Ni/CaO/Fe₂O₃-MgAl₂O₄.^[51] Two oxidants help distinguish Ni and Fe oxidation steps. Iron oxidizes to Fe₂O₃ starting at 400 °C with a doublet at 615–665 °C with CO₂ as an oxidant. With O₂, the oxidation starts at 90 °C with a two prominent peaks at 100 °C and 160 °C. These experiments also clarify oxygen uptake from CO₂ and oxidation kinetics in bimetallic systems.

Researchers also studied Fe–Ni–Al–O oxygen carriers using TPO after TPR. They identified separate surface (α) and bulk (β) reoxidation peaks. Scaling the material from laboratory powder to industrial beads shifted both peaks to higher temperatures, indicating increased diffusion and kinetic limitations during oxidation.^[52]

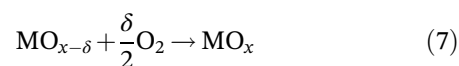
In situ TPO combined with X-ray techniques has also distinguished active Fe₂(MoO₄)₃ phases from inactive Fe-rich domains in methanol oxidation catalysts. Low-temperature peaks correspond to oxidation of reduced iron (Fe²⁺) and MoO₂, whereas higher-temperature peaks restore the mixed oxide structure and regenerate active catalyst phases.^[53]

TPO also quantifies copper surface area and oxidation behaviour in Cu-based catalysts. Pre-reduced copper exposed to diluted N₂O selectively oxidizes the surface copper to Cu₂O and produces N₂. Researchers determined the copper surface area based on how much N₂ was released.^[54] Low-temperature peaks indicate oxidation of dispersed surface atoms, whereas high-temperature peaks correspond to bulk oxidation.^[55]

We also use TPO to study oxidation, redispersion, and regeneration of noble-metal catalysts. Oxidative treatments redisperse sintered metal particles to smaller clusters, restoring catalytic activity and surface area. Temperature, oxidation conditions, and support properties influence the extent of redispersion.^[56]

2.3.3 | Re-oxidation of defective oxides

In defective oxides, TPO measures oxygen uptake associated with filling oxygen vacancies and restoring the oxide lattice:

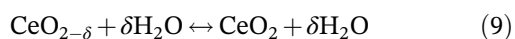
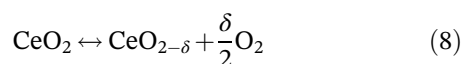


The release and re-oxidation characteristics of non-stoichiometric perovskites provide information about their oxygen vacancy formation energy and oxygen mobility. For example, cyclic H₂-TPR/O₂-TPO experiments on LaCoO₃ can probe oxygen removal, oxygen-vacancy formation, and the generation of reduced Co species, such as La₂CoO₄ or Co/metal oxide. During the oxygen dosing of TPO, oxygen re-inserts into the lattice and oxidizes the Co. Replacing A or B sites in an ABO₄ perovskite structure with other cations like Sr₃⁺, doped LaCoO₃, or LaFeO₃ enhances the oxygen uptake/release.^[57]

Cyclic TPR/TPO dosing of spinels or high-entropy oxides heals the materials as they recover their oxygen loss and regain performance. Mg–Fe–Al spinel (MgFeAlOx) is an example of a stable compound with a reversible lattice oxygen capacity. Based on in situ XRD during intermittent TPR and CO₂-TPO, the structure was maintained over multiple hydrogen reduction/CO₂ oxidation cycles, with negligible sintering. Spinel can reoxidize and reduce numerous times, suggesting that the

lattice oxygen is mobile and robust.^[58] Perovskite materials such as $\text{La}_{0.5}\text{Ba}_{0.5}\text{FeO}_3$ show similar oxygen uptake and vacancy healing behaviour, with oxidation peaks distinct from reduction peaks.^[59] Substituting cations enhances oxygen vacancy formation and oxygen mobility.^[57]

TPO also applies to reducible oxides such as cobalt oxide and ceria. For cobalt oxides, TPO identifies oxidation steps such as $\text{CoO} \rightarrow \text{Co}_3\text{O}_4$, confirming reversible oxygen mobility. Ceria's remarkable oxygen storage capacity originates from its ability to form oxygen vacancies. It undergoes reversible redox cycles by releasing oxygen from the oxide lattice and then recapturing it during reoxidation or water splitting:



Low-temperature peaks correspond to oxidation of surface Ce^{3+} sites, whereas high-temperature peaks correspond to oxidation associated with bulk oxygen vacancies.^[60–62] These reactions enable oxygen release and reincorporation, which is essential for redox catalysis and hydrogen production.^[13] These results confirm that cobalt oxides and ceria are promising oxygen carriers for thermochemical hydrogen production.

2.4 | Detectors

2.4.1 | Thermal conductivity detector

A thermal conductivity detector (TCD) measures changes in the thermal conductivity of the effluent gas relative to a reference gas stream. We set the reference-gas flow rate and composition to match those of the carrier gas. For this reason, we typically supply both streams from the same gas cylinder and control each flow with accurate mass flow controllers. We also maintain isothermal conditions between the carrier and reference streams: both gases must reach the detector at the same temperature.

TCD is non-selective and non-destructive, and it responds to essentially any gas. Any species with a thermal conductivity different from the reference gas, or oxygen consumption that reduces the outlet O_2 level, changes the measured signal.^[63] As a result, TCD cannot resolve individual species when multiple gases overlap in the signal.

The TCD detection limit typically lies between 50 and 500 ppm.^[64] TCD response remains approximately linear

over four to five orders of magnitude (10^4 – 10^5), spanning from low-ppm to percent-level concentration. Detector sensitivity depends strongly on the inert gas used in the carrier mixture. Helium and hydrogen are the preferred diluents because their conductivities are $>5\times$ higher than most other gases.

2.4.2 | Mass spectrometer (MS)

An inline quadrupole mass spectrometer (MS) continuously samples the TPO reactor outlet gas under vacuum and reports ion currents at selected mass-to-charge (m/z) ratios. MS provides fast and sensitive detection and, unlike TCD, offers excellent selectivity. It tracks oxygen uptake and oxidation products by monitoring appropriate m/z ratios for specific species and their isotopes.

Unlike TCD, which is incapable of resolving overlapping peaks from different species, MS selectively distinguishes individual compounds and identifies reaction pathways through isotopologue detection. In kinetic studies such as dry methane reforming (DRM), coupling MS with isotopically labelled reactants and subsequent TPO identifies the carbon source.

For example, using $^{13}\text{CO}_2$ and $^{12}\text{CH}_4$ during DRM and monitoring ion currents during TPO revealed only $^{12}\text{CO}_2$ after carbon oxidation. This result confirmed that deposited carbon originated from CH_4 . Similarly, the detection of C^{18}O during DRM pulses showed that oxygen originated from CO_2 rather than the lattice.^[50]

Some gases share identical m/z values, such as N_2 and CO ($m/z = 28$) or N_2O and CO_2 fragments. In addition, electron ionization fragments molecules, causing CO_2 to produce signals not only at $m/z = 44$ but also at $m/z = 28$ and 16.

To avoid misassigning species, MS analysis should include at least one confirmer ion in addition to the primary ion (Table 2). This approach is particularly important when oxidation products include complex mixtures of C^- , N^- , or S^- containing species. Although MS can operate with different carrier gases, He is best. It is easily identified due to its unique m/z signal and minimal fragmentation interference. In contrast, the overlap at $m/z = 28$ between N_2 and CO complicates accurate carbon quantification. Multi-level calibration using certified gas mixtures helps determine instrument response factors and fragmentation patterns.

MS identifies signals that are sufficiently different from background noise. With an electron multiplier detector, the detection limit is down to the order of 100 ppb.^[5]

TABLE 1 Gas thermal conductivity (in mW m⁻¹ K at 25 °C).

Gas	<i>k</i>	Gas	<i>k</i>
H ₂	187	H ₂ O	18.6
He	156	Ar	17.7
O ₂	26.5	N ₂ O	25.3
N ₂	26.0	CO ₂	16.8
NO	25.9	SO ₂	9.6
CO	25.0		

TABLE 2 Recommended *m/z* channels and confirmers for quadrupole mass spectrometers monitoring during temperature-programmed oxidation.

Species	<i>m/z</i>	Confirmers
O ₂ (oxidant)	32	16 (O ⁺)
H ₂ O	18	17 (OH ⁺)
CO	28	29 (¹³ CO/fragment), 12
CO ₂	44	45 (¹³ CO ₂), 46 (C ¹⁸ O)
N ₂ (matrix)	28	14
SO ₂	64	48, 66
NO	30	—
NO ₂	46	30
N ₂ O	44	30 (fragment)
¹³ CO (isotope)	29	—
¹³ CO ₂ (isotope)	45	46

2.4.3 | FID detectors (methanation)

A methanator placed downstream of a TPO u-tube and coupled to a flame ionization detector (FID) quantifies carbon content.^[7,65] The methanator with a Ni- or Ru-based catalyst converts carbon oxides to methane.

Compared with TCD and even TGA, FID offers higher sensitivity (<0.003 g g⁻¹), better precision, and superior signal resolution. The carrier gas enters the methanator that hydrogenates CO and CO₂, formed during carbon oxidation, to CH₄ at 400 °C. The detector continuously monitors methane generated but remains insensitive to O₂ and H₂O. However, when high water concentrations evolve, an elevated O₂ concentrations in the carrier gas reduces methane efficiency, thereby limiting the optimal carrier flow rate, which typically lies between 20 and 60 mL min⁻¹. Under such conditions, operating at higher temperature maximizes carbon oxide conversion to CH₄.

When the O₂ concentration exceeds 3%, an oxygen trap installed upstream of the methanator ensures complete conversion of CO and CO₂.^[5] FID can detect less than 10⁻⁹ g of hydrocarbons.^[47]

2.4.4 | IR detectors

Non-dispersive infrared (IR or NDIR) detectors are non-destructive techniques to measure gas concentration through absorption of infrared radiation by specific molecules. When coupled to TPO systems, IR detectors quantify in real-time CO₂. LECO carbon analyzer, for example, converts CO to CO₂ above 1300 °C and an IR detector monitors the CO₂ concentration.^[4,6,8] IR detectors are also appropriate for sulphur species. SO₂ has strong and characteristic IR absorption bands. We apply the Lambert–Beer law to interpret the bands.^[4,66] IR precision resolution reaches 1 µg g⁻¹ and an error below 0.5%, which is better than a TCD.^[66,67] Moreover, it is better suited for complex solid matrices, which may contain multi-elemental interference or very low sulphur concentrations.

Pre-filtration of water and interfering gases further improves selectivity. The direct correlation between peak intensity and sulphur content provides higher accuracy than semi-quantitative surface techniques such as XPS and EDS. Most NDIR analyzers operate at a specific absorption wavelength assigned to a single compound. In addition, homonuclear and symmetric molecules such as O₂ do not absorb IR radiation and therefore remain invisible to NDIR and FTIR detectors.

3 | APPLICATIONS

In the last 5 years, 2021–2025, WoS has indexed 1842 articles on TPO. Many of these articles also reference TPR (51 occurrences), temperature-programmed desorption—TPD (71), and temperature-programmed surface reaction—TPSR (12).^[64,68] The top 5 most prolific scientific categories are physical chemistry with 735 articles, then chemical engineering (540), energy & fuels (317), multi-disciplinary chemistry (287), and multidisciplinary materials science (281). Coincidentally, the most prolific journals are: *Catalysts* with 94 articles, followed by *Fuel* (83), *ACS Catalysis* (52), *Catalysis Today* (52), *Chemical Engineering Journal* (50), and *Journal of Physical Chemistry C* (50).

Since 2023, *The Canadian Journal of Chemical Engineering* has published three articles that deal with kinetics derived from thermogravimetric analysis and ball milling, removing Hg from flue gas, and hydrogenation of oleic acid: “Thermogravimetric Kinetic Analysis of the Ce–Zr Composite Oxygen Carrier Prepared by Ball Milling”,^[69] “Mn_{3-x}Cr_x-LDO, A New Sorbent, for Efficient Elemental Mercury Removal from Coal-Fired Flue Gas”,^[70] and “Selective Hydrogenation of Oleic Acid to Fatty Alcohols Using Rh-Sn-B/TiO₂ catalysts: Influence of Sn content”.^[71] *ACS*

Catalysis published the three most cited papers “Engineering Cobalt Oxide with Coexisting Cobalt Defects and Oxygen Vacancies for Enhanced Catalytic Oxidation of Toluene” (290 citations),^[72] “Morphology Effects of CeO₂ Nanomaterials on the Catalytic Combustion of Toluene: A Combined Kinetics and Diffuse Reflectance Infrared Fourier Transform Spectroscopy Study”,^[73] and “Interfacial Engineering of Ni₃N/Mo₂N Heterojunctions for Urea-Assisted Hydrogen Evolution Reaction”. Most of these articles involve catalysis.

Here, we developed a bibliographic map with the online, open access program (VOSViewer) based on the search criterion “temperature program” oxidation in WoS (Figure 4).^[74,75] VOSviewer categorized the 102 keywords into four clusters based on how often they appear together (co-occurrences): the red cluster has 39 keywords and is centred on **catalyst** and **hydrogen**. The green and blue clusters each have 26 keywords and **oxidation (oxid’n)** and **oxide** have the most mentions. NO_x in the

yellow cluster occurs most frequently and there are only 11 keywords in the cluster.

The Ni and Cu are the metals most often mentioned in the data base with 173 and 118 occurrences while the least mentioned are Au, Ru, and Ce with 30 mentions: Ni > Cu > Mn > Pt > Pd > Fe > Co > Rare Earth > Au > Ru > Ce. The ranking for the supports is: CeO₂ (202 articles), zeolite (149-ZSM5 and others), TiO₂ (90), perovskite (64), Al₂O₃ (56), and ZrO₂ (33). Ni, Pt, and Pd are most associated with H₂, methane, and CO₂ and selective/partial oxidation and hydrogenation Table 3. Selective catalytic reduction goes with Cu and zeolite supports for NO_x, NH₃, and SO₂.

TPO combined with TPR removes contaminants, probes catalyst reactivity, redox properties, and the percentage of the active metal phase.^[76,77] Although TPO is less common, it is more accurate in quantitation than TPR.^[21] Only TPO detects the peak of graphitic coke, which requires temperatures beyond those typical of

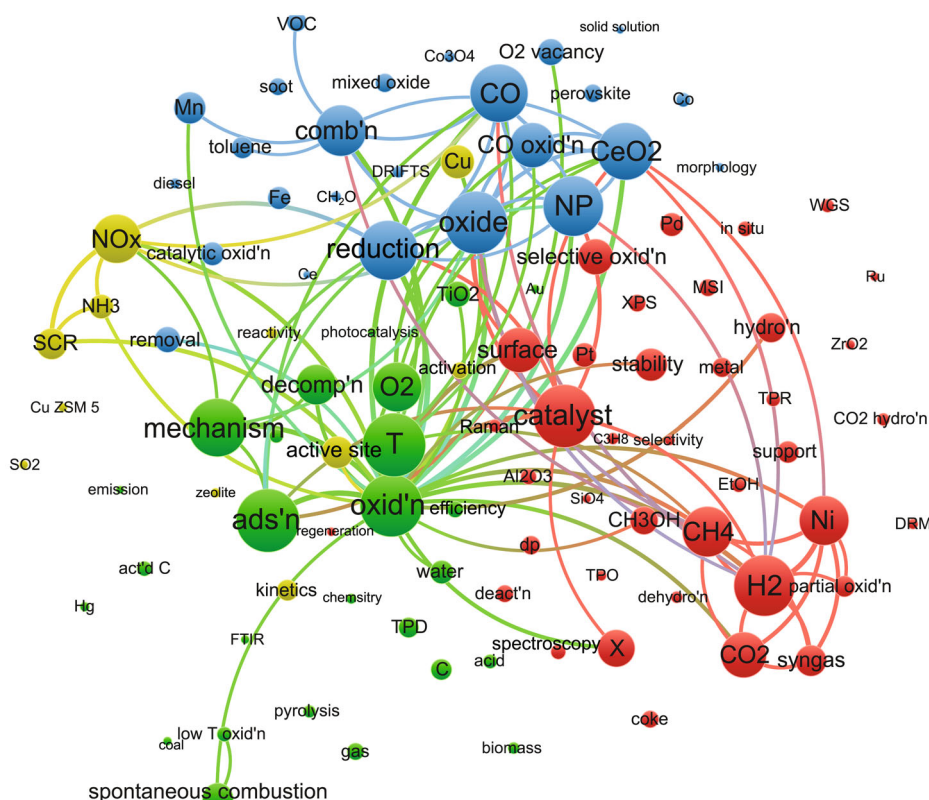


FIGURE 4 Temperature-programmed oxidation bibliometric map of the 102 most mentioned keywords of 1842 articles that WoS indexed from 2021 to 2025.^[74,75] The nodes correspond to how many times a keyword appears in the articles: The smallest nodes represent 29 occurrences (Ce, emission, solid solution) while the largest represent over 220 mentions (T, for example.) Oxidation (oxid’n) in the green cluster has 578 mentions but we assigned it a value of 220 to minimize overlap with other nodes. The keywords **catalyst** and **oxide** were also rescaled from 273 and 268, respectively, to 220. Abbreviations: act’d C, activated carbon; act’n, activation; ads’n, adsorption; comb’n, combustion; deact’n, deactivation; decomp’n, decomposition; dehydro’n, dehydrogenation; DFT, density function theory; dp, particle size; DRIFTS, diffuse reflectance infrared fourier transform spectroscopy; DRM, dry reforming of methane; FTIR, Fourier transform infrared; hydro’n, hydrogenation; MSI, metal-surface interaction; NP, nanoparticle; oxid’n, oxidation; regen’n, regeneration; SCR, selective catalytic reduction; T, temperature; WGS, water gas shift; X, conversion; and, XPS, x-ray photoelectron spectroscopy.

TABLE 3 Reaction classes, compounds, and catalysts/supports cited in the clusters of Figure 4. For every column (and cluster), the order proceeds from keywords mentioned most often to the least, which correlates with cluster size of the figure.

Reaction	Compound	Catalyst/support
Selective oxidation	H ₂	Ni
Hydrogenation	CH ₄	Pt
Partial oxidation	CO ₂	Pd
Water gas shift	Syngas	Al ₂ O ₃
CO ₂ hydrogenation	CH ₃ OH	ZrO ₂
Dehydrogenation	Coke	Ru
Methane dry reforming	EtOH	SiO ₄
Regeneration	C ₃ H ₈	
Oxidation	O ₂	
Decomposition	Water	TiO ₂
Spontaneous combustion	C	Activated C
low <i>T</i> oxidation	Biomass	Hg
Pyrolysis	Coal	Au
Photocatalysis		
	CO	CeO ₂ /Ce
Reduction	Toluene	Mn
Combustion	VOC	Fe
CO oxidation	Soot	Perovskite
Catalytic oxidation	CH ₂ O	Co/Co ₃ O ₄
	Diesel	Rare earth
	NO _x	Cu
Selective catalytic reduction	NH ₃	Zeolite
	SO ₂	Cu ZSM 5

TPR.^[30] Researchers are combining TPOs with other analytical techniques. From the cited keywords indexed by WoS in 2025, the order and number of articles are: TPD (71 articles), XPS (60), spectroscopy (54), TPR (51), Raman (45), DRIFTS (41), FTIR (31), IR (26), XRD (19), TPSR (12), and XAS (10).

TPO also applies in the study of oxidation of nitrogen,^[78] coal desulphurization^[79] and oxidation states of metals,^[77,80] (spontaneous) combustion, and (CO₂) hydrogenation.

Coupled with XRD,^[81] TPO identified multiple carbon domains with different atomic organizations (the lower the structural order, the lower the peak oxidation temperature in the TPO profile).^[82] TPO is also a reliable, fast, and quantitative technique to analyze soot traces on different substrates generated by thermal stress tests of jet-fuels.^[31,83] The catalytic coke formation followed Ni > SS316 > SS304 and the temperature corresponding to

the main peak identified the type of coke formed during the thermal degradation. Aso et al. employed TPO as an analytical technique to measure the size of anthracite graphene sheets.^[84] From the deconvolution of the peaks of CO, CO₂, and H₂O samples heated at 2 K min⁻¹, they identified the elemental composition of the organic fraction and also the aromatic content of the graphene samples.^[84] Montero et al.^[46] studied the nature of coke over Ni/La₂O₃-αAl₂O₃ catalyst in ethanol steam reforming (ESR) as a function of space velocity: amorphorous coke on metal sites reacted below 450°C. Above 450°C, coke with a higher aromaticity, fibrillar structure, and varied graphitization degree distant from the metal sites reacted.

4 | SOURCES OF ERROR

Experimental conditions—sample concentration (metal or coke), morphology, particle size and mass, heating rate, flow rate, oxygen concentration—modify TPO profiles. High heating rate shortens the analysis time and increases the sensitivity. The peak temperature of a coked catalyst is 37°C higher at heating rate of 25 than 7°C min⁻¹.^[47] The area corresponding to mass of CO₂ and temperature of the start of the peak were same. As in TPR, heat-transfer limitations can constrain the maximum usable heating rate.

To minimize spurious signals, such as noise and false peaks, and to remove decomposable or catalytic materials, samples are pre-treated and traps are installed to remove known contaminants.^[21] Dosing the sample with 1–5% H₂ in He is standard. Pre-treating Co/Al₂O₃ below 375°C and calcining in pure H₂ minimizes metal-support sintering.^[21] The emission patterns are independent of the coal organic and pyritic sulphur contents, however, they depend on experimental conditions and coal pre-treatment (acid washing, organic solvent extraction, low temperature ashing).^[79]

Frequent calibration of the detectors is also necessary. The integrated area under the peak corresponds to the O₂ consumed. To account for baseline drift of the TCD profile, we apply a linear model with data in the range from 10°C to 30°C^[80] and calibrate the CO and CO₂ signals with calcium oxalate monohydrate (CaC₂O₄ · H₂O). Compared with the combustion analysis results from Galbraith laboratories, errors are within 5%.^[27] The amplitude of MS signal is proportional to the gas evolution rate. Slowly degassing, connections and piping, MS capillary length, and the MS analysis chamber modify the response coefficients. When the residual water concentration is high, Boudou recommends recalibrating the MS every five to ten experiments.^[79]

4.1 | Detection limits

TCD senses the difference of thermal conductivity between the effluent gas and the reference flow of carrier gas, which is inexpensive to setup and easy to operate. It detects target gas concentration ranges from 0.005‰ to 0.05‰.^[64] However, the detection of CO₂ via TCD is discontinuous as it requires to separate CO₂ from O₂ via a gas chromatography (GC) column.

MS detector requires a minimum component partial pressure depending on its mass. MS identifies signals that are sufficiently different from background noise. With electron multiplier detector, detection limit is down to the order of 100 ppb.^[85]

4.2 | Case studies

To gauge repeatability of the TPO technique, we conducted experiments in an Altamira AMI-300HP instrument equipped with multiple mass flow controllers, a linear μ -TCD with tungsten filaments, and control software to automate the data acquisition (Figure 1). An electric furnace heated samples in a quartz U-tube and ramped temperature at a prescribed rate. Together with the μ -TCD, we monitored multiple species from the effluent with a HIDEN QIC-20 mass spectrometer equipped with a Faraday detector. Nickel-on-alumina/silica was chosen (0.65 g g⁻¹ Ni-P/N: 208779, Sigma-Aldrich) as a model catalyst to differentiate oxygen consumption from gas evolution.



XRD patterns indicated that metallic Ni is the dominant phase, with a minor amount of Al₂O₃, and no detectable carbonaceous species (Figure 5). Therefore, the TCD and MS responses reflect oxygen consumption only, which facilitates interpreting the detector signals.

The thermal conductivity of He is an order of magnitude greater than Ar (Table 1), and this difference makes a tremendous difference in the TCD signal intensity, polarity and stability (Figure 6). The profiles rise at approximately the same temperature and reach a maximum within 50 °C of each other. We could hypothesize that the intrinsic reaction is independent of carrier gas but the data is sufficiently different to warrant further testing. The differences arise from the operating principle of the TCD, whose sensitivity depends on the thermal-conductivity contrast between the carrier gas and the reacting species. Because helium exhibits a substantially higher thermal conductivity than oxygen, helium-based

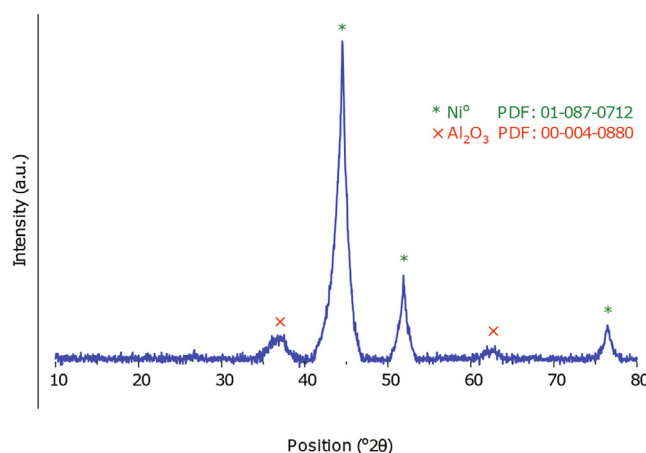


FIGURE 5 The X-ray diffraction profile of the nickel-based sample used in this study.

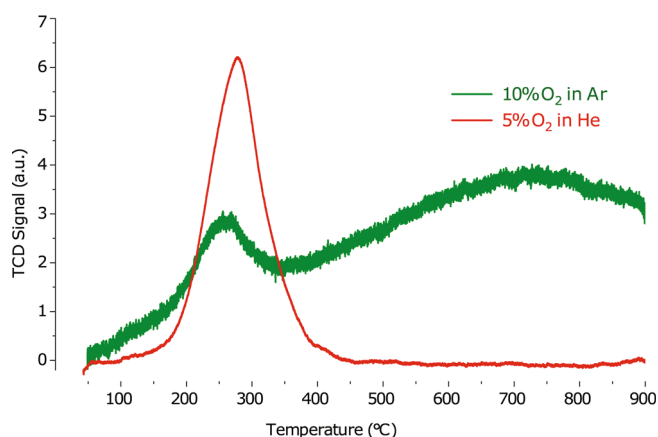


FIGURE 6 Temperature-programmed oxidation profiles with He versus Ar as a carrier gas: Heating rate of 10 °C min⁻¹, Q = 50 mL min⁻¹, y_{O₂} = 0.05, m_{Ni/Al₂O₃} = 40 mg.

TPO measurements produce a larger detector response. The lower thermal-conductivity difference between argon and oxygen decreases signal stability, resulting in larger baseline fluctuations and broader, noisier peaks. In addition, in helium-based TPO tests, oxygen consumption generates negative peaks in the TCD signal, whereas argon-based TPO produces positive peaks due to the opposite direction of the thermal-conductivity change. For clarity and consistency, unless otherwise stated, all helium-based TPO traces in this study are inverted; this operation does not affect the physical interpretation of the oxidation behaviour.

The moles of oxygen consumed, n_{O_2} , per gram of sample, m_s is proportional to the product of the oxygen molar concentration, $y_{\text{O}_2}P/(RT)$ and sample volume, V_{loop} , multiplied by the ratio of the area under the TPO curve, A_{TPO} and the calibration curve, A_{loop} :

$$n_{O_2} = \frac{1}{1000} \frac{y_{O_2} P}{RT} \cdot \frac{V_{loop}}{m_s} \cdot \frac{A_{TPO}}{A_{loop}} \quad (\text{mmol g}^{-1}) \quad (11)$$

The shape of the TPO curves are independent of the carrier gas flow rate, $Q_{carrier}$ (Figure 7): However, with increasing, $Q_{carrier}$ the TCD peak intensity decreased since more oxygen was delivered to the metallic sites but it had negligible impact on the calculated oxygen uptake, n_{O_2} ; it decreased only slightly from $1884 \mu\text{mol g}^{-1}$ at $Q = 50 \text{ mL min}^{-1}$ to $1822 \mu\text{mol g}^{-1}$ at $Q = 200 \text{ mL min}^{-1}$, a difference of 3%. This error is likely attributable to the uncertainty in calculating V_{loop} : the volume is smaller for $Q = 200 \text{ mL min}^{-1}$ on the one hand, but on the other hand, the signal increases at a lower temperature for $Q = 50 \text{ mL min}^{-1}$. Under these conditions, the Ni oxidation rate is kinetically controlled and depends on temperature and the availability of metallic sites. Because the TCD signal responds to changes in gas composition (and thus thermal conductivity) rather than to the absolute amount of oxygen consumed, higher flow rates mainly introduce hydrodynamic dilution that lowers peak intensity. Therefore, the reduced TCD signal at elevated flow rates reflects a dilution effect, whereas the overall oxygen uptake remains governed by the catalyst's intrinsic redox capacity.

The heating-rate tests confirm that the reaction rate is kinetically controlled rather than mass-transfer controlled, as the curve shapes are invariant in the range of $5\text{--}20^\circ\text{C min}^{-1}$ (Figure 8). The oxidation peaks are higher and the maximum temperatures shift somewhat to the right to higher temperature. We attribute this trend to the higher temperature reached at a given time under

faster ramps, which increases the instantaneous oxidation rate and accentuates peak shape and amplitude changes. Consistently, the calculated oxygen uptake increased with heating rate, indicating higher apparent oxygen consumption at higher ramps. However, for complex samples that undergo multiple oxidation processes (e.g., carbon burn-off, metal oxidation, and decomposition), higher heating rates reduce peak resolution and increase thermal lag between the sample and furnace, which may cause partial overlap of oxidation events.

The nickel-containing sample shows a clear mass-dependent response in the TPO profiles (Figure 9). Under identical conditions (heating rate of $10^\circ\text{C min}^{-1}$ and $Q = 50 \text{ mL min}^{-1}$), increasing the sample mass progressively increased the TCD peak intensity, consistent with a larger number of oxidizable metal sites. In contrast, the peak maximum remained essentially unchanged across the investigated masses: the highest was lower by 20°C but the other three hovered around 285°C . All peaks were similar in shape, indicating that mass- and heat-transfer limitations were negligible. Nevertheless, when complex samples exhibit multiple oxidation events, peaks overlap with larger samples and thus reduce the resolution.

TPO curves of five repeat experiments were essentially identical with $n_{O_2} = 1884 \mu\text{mol g}^{-1}$ and $\sigma = \pm 18 \mu\text{mol g}^{-1}$ (Figure 10). The oxygen signal for all of the tests increased at the same temperature, reached the maximum signal at the same temperature, and dropped to the baseline at the same temperature.

For carbon-containing samples, oxygen reacts to form CO and CO_2 simultaneously. The TCD response when O_2 is consumed is negative with helium as a carrier because it lowers the overall thermal conductivity of the outlet

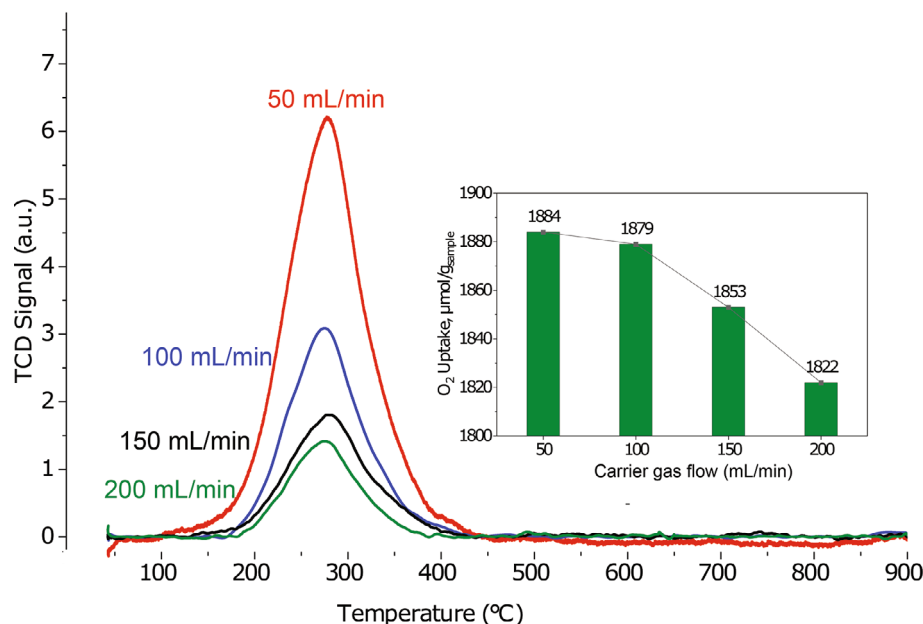


FIGURE 7 Temperature-programmed oxidation profiles as a function of carrier gas flow rate, Q at a heating rate of $10^\circ\text{C min}^{-1}$ with $y_{O_2} = 0.05$ in He.

FIGURE 8 Temperature-programmed oxidation profiles as a function of heating rate at $Q = 50 \text{ mL min}^{-1}$ and $y_{\text{O}_2} = 5\%$ in He. The maximum heat rates rise slight with increasing heating rate: $T_{\text{max},5} = 265^\circ\text{C}$, $T_{\text{max},10} = 275^\circ\text{C}$, $T_{\text{max},15} = 285^\circ\text{C}$, and $T_{\text{max},20} = 281^\circ\text{C}$.

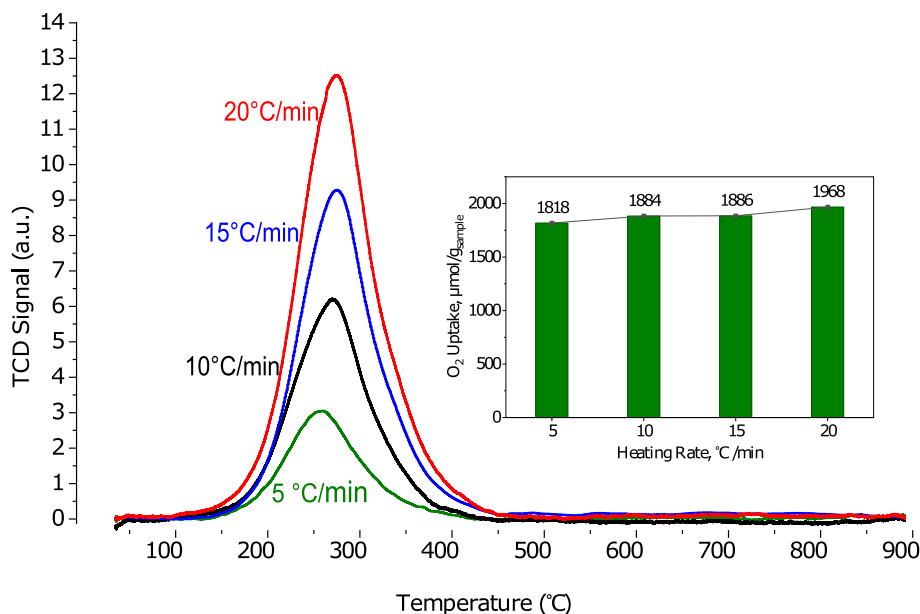
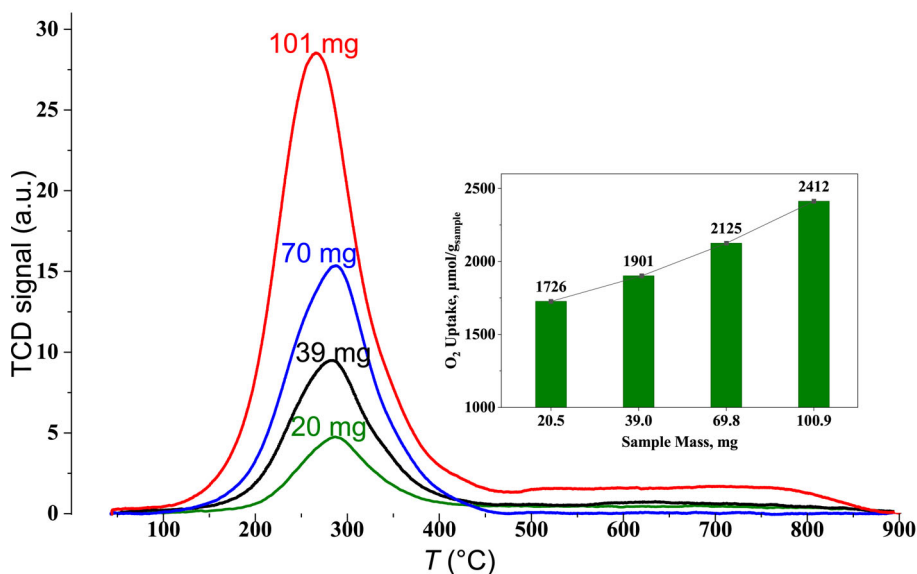


FIGURE 9 Temperature-programmed oxidation profile shape as a function of sample mass, m_s , at a ramp of $15^\circ\text{C min}^{-1}$, $Q = 50 \text{ mL min}^{-1}$, and $y_{\text{O}_2} = 5\%$ in He.



gas, whereas it is positive when carbon oxides evolve. Consequently, the measured TCD trace represents the net contribution of oxygen uptake and gas evolution rather than a pure oxidation signal. We deposited carbon on the nickel-containing sample by carrying out methane decomposition in an Inconel 600 reactor. We loaded 10 g of catalyst, heated the reactor to 900°C , and maintained this temperature for 2 h while feeding 25% CH_4 diluted in N_2 . Under these conditions, the sample accumulated 0.394 g g^{-1} carbon, as determined by LECO CS 744 analysis. The CO and CO_2 signals dominates the TCD response, which overwhelms the negative oxygen peak in the case of a simple oxidation yields (Figure 11). We simultaneously monitored the MS signals for CO, CO_2 , and O_2 ($m/z = 28$, 44, and 32, respectively). As

temperature increased, we detected a broad and weak negative TCD feature between 400°C to 500°C , accompanied by only a small decrease in the O_2 MS signal and negligible changes in the CO and CO_2 signals. We attribute this region to limited oxidation of metallic nickel. The shift of the nickel-oxidation feature to higher temperature, together with the reduced oxygen uptake in this region, suggests that a nickel-support solid-state oxide reaction may hinder nickel oxidation. At higher temperatures, the TCD trace displayed a positive, asymmetric peak while the CO and CO_2 MS signals rose and the corresponding O_2 signal declined. Although oxygen consumption continued, the concurrent evolution of CO and CO_2 offset the negative contribution from oxygen uptake, producing an overall positive TCD response. This

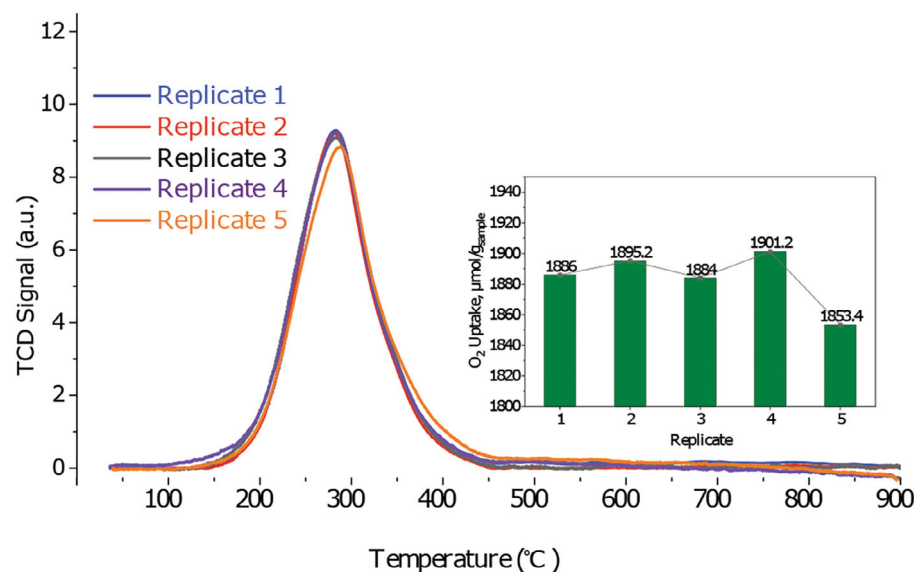


FIGURE 10 Temperature-programmed oxidation repeatability tests at a ramp of $15^{\circ}\text{C min}^{-1}$, $Q = 50\text{ mL min}^{-1}$, $y_{\text{O}_2} = 5\%$ in He, and $m_s = 40\text{ mg}$.

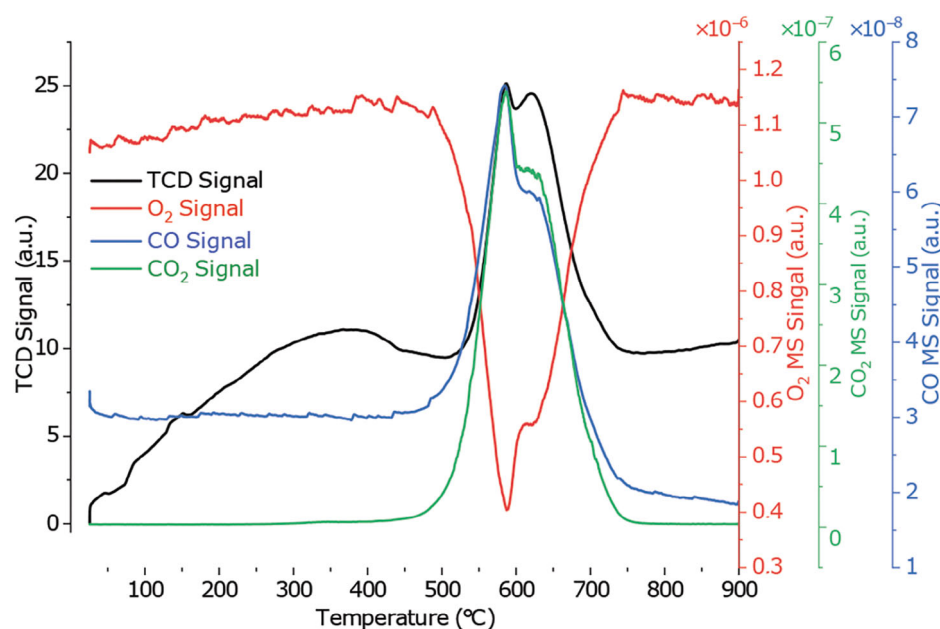
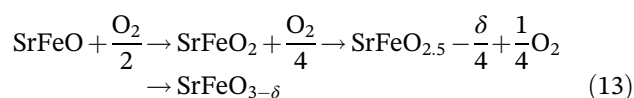
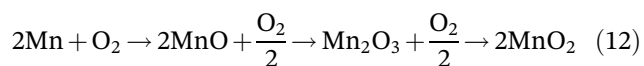


FIGURE 11 Thermal conductivity detectors and mass spectrometers temperature-programmed oxidation profiles of spent catalyst ($m_s = 41.2\text{ mg}$) at a heating rate of $5^{\circ}\text{C min}^{-1}$ and a carrier gas flow rate of 50 mL min^{-1} .

superposition highlights the need to couple TPO with mass spectrometry to interpret oxidation behaviour reliably, particularly for carbon-containing catalysts. The CO and CO₂ signals returned to baseline at approximately 750°C , indicating complete carbon burn-off; concurrently, the O₂ MS signal recovered to its pre-oxidation level, confirming the end of carbon oxidation.

Carbon complicates interpreting TPO curves and another complication arises from metals with multiple oxidation states, like Mn and perovskites, like SrFeO_{3-δ}:



These materials are candidates as an oxygen source for cyclic redox processes.

Before reduction, the TPO curve for a SrFeO_{3-δ} perovskite, prepared using a method of solid-state ball milling (lower blue curve Figure 12 and expanded view in the inset),^[86] is somewhat flat with only subtle features. The perovskite consumed some oxygen below 300°C . It released oxygen via uncoupling up to 800°C —the inverted TPO peak corresponds to 0.56 mmol g^{-1}

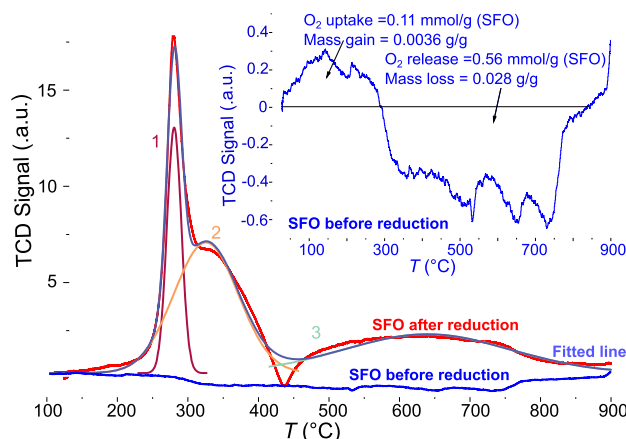


FIGURE 12 SRO TPO profiles before reduction (blue line and inset) and after reduction (red line) with 10% H_2 , and at a ramp of $10^\circ C\ min^{-1}$ (TCD signal). We calculate the oxygen uptake and release ($mmol\ g^{-1}$ of SRO) assuming the baseline remains at 0 across the entire ramp (no baseline drift). Three Gaussian curves approximate the TPO signal well ($R^2 = 0.986$) but ignore the dip at $430^\circ C$. With complementary analytical capability, we could establish whether the dip was a spurious signal or due to physico-chemical phenomena. If the three peaks correspond to the change in oxidation state from $SrFeO$ to $SrFeO_{2.6}$, we would have expected the first peak (1) to be much larger than the either (peak 2) or (peak 3). The best fit line is in blue-purple.

($0.018\ g\ g^{-1}$, 1.8% by mass) or $\Delta\delta = +0.2$. This value agrees with previous measurements heating $SrFeO_{3-\delta}$ in air.^[86] The estimated oxygen uptake and release are sensitive to the assumed baseline: A constant baseline at 0 a. u. that extends across the entire temperature range overestimates $\Delta\delta$ when, in fact, the base line drifts upwards.

After reducing the perovskite in 10% H_2 (ramping from room temperature to $900^\circ C$), re-oxidizing in air produces a TPO curve with three distinct features. The first sharp peak starts at $250^\circ C$ with a shoulder extending to $400^\circ C$. The third feature is a broad peak extends from 450 to $800^\circ C$. The total oxygen uptake is $4.9\ mmol\ g^{-1}$ 15.6% by mass and $\Delta\delta = -1.6$. A change of 1.6 in the oxygen stoichiometry suggests that the chemical formula of the perovskite after the reduction step was $SrFeO$, that is, a mixture of SrO and metallic Fe . The final oxygen stoichiometry is consistent with previous measurements of $SrFeO_{3-\delta}$ brought to equilibrium with $P_{O_2} = 0.1\ atm$ at $900^\circ C$.^[87] Coupling the TPO experiments with XRD would confirm that the peaks correspond to the intermediate phases forming (e.g., Ruddlesden–Popper $Sr_{n+1}Fe_nO_{3n+1}$ or Brownmillerite $SrFeO_{2.5}$), and the final oxidation state.^[86,88]

These experiments highlight the possible variability introduced by changing the reduction and oxidation conditions for complex materials: A faster ramp

would be insufficient to produce $SrFeO$, for example, or to re-oxidize it to $SrFeO_{2.6}$. In a redox process, the SRO oxygen cycle would be much less than $\pm\Delta\delta = 1.6$. Identifying the stoichiometric range of the SRO requires complementary analytical equipment as well as multiple cycles. In this example, the reaction starts at low temperature, but for a process operating at $800^\circ C$ would the redox couple vary from $SrFeO$ to $SrFeO_{2.6}$ or some intermediate oxidation state? The reaction kinetics would necessarily account for the relationship between the various oxidation states, activation energies, and reaction rates.

5 | CONCLUSIONS

TPO is a versatile characterization tool that identifies how fast and at what temperature catalyst, coke and other carbonaceous materials, defective oxides, and reduced metals react with oxygen. TPO distinguishes carbon species according to their oxidation temperatures, helping identify coke type, distribution, reactivity, and burn-off behaviour. It also tracks metal reoxidation processes and to derive reaction kinetics and the extent of oxide formation in supported metal catalysts. Based how the effluent concentration of oxygen changes as a function of the time/temperature history in the powder bed, we deduce material surface activity, redox properties, catalyst deactivation pathways, and various forms of coke. Carrier gas composition, flow rate, heating rate, and sample mass modify peak shape and intensity, and directly affect the interpretation of oxidation kinetics, oxygen uptake, and surface reactivity. Rigorously controlling the operating parameters—temperature ramp, flow rate, powder mass—assures an experimental repeatability approaching 1%. For complex systems containing multiple species, a TCD is insufficient to resolve the peaks particularly when they overlap. On-line mass spectrometry is best for these conditions but even so, several m/z signals are confounded like CO and N_2 . Combining TPO with temperature-programmed reduction (TPR) and other complementary analytical techniques such as thermogravimetry (TG), modulated thermogravimetry (MTG), FTIR-MS, Raman spectroscopy, and differential scanning calorimetry (DSC) improves our capability of characterizing the chemistry. These integrated approaches identify the nature and location of coke, clarify combustion pathways, reveal structural features of deposited carbon, and support the design of more effective catalyst regeneration strategies. TPO research will continue to expand by integrating it with other spectroscopic techniques like in-situ XRD, SEM/TEM, and perhaps magnetometry.

AUTHOR CONTRIBUTIONS

Gholamreza Roohollahi: Conceptualization; data curation; formal analysis; methodology; writing – review and editing; writing – original draft; visualization. **Jildimara de Jesus Santana:** Conceptualization; data curation; formal analysis; visualization; methodology; investigation; validation; writing – review and editing; writing – original draft. **Alexander R. P. Harrison:** Conceptualization; data curation; formal analysis; visualization; investigation; methodology; validation; writing – original draft; writing – review and editing. **Sara Andreoli:** Conceptualization; investigation; writing – original draft; methodology; visualization; writing – review and editing. **Ewa Marek:** Supervision; writing – review and editing; formal analysis; validation. **Stuart Scott:** Supervision; writing – review and editing; validation. **Mohammad Latifi:** Supervision; writing – review and editing. **Gregory S. Patience:** Data curation; conceptualization; methodology; investigation; supervision; formal analysis; visualization; writing – original draft; writing – review and editing; project administration.

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PEER REVIEW

For transparency, the peer review documents associated with this article are available at <https://doi.org/10.1002/cjce.70527>.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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