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Supporting Information

Coke Formation during Propane Dehydrogenation over Ga–Rh Supported Catalytically Active Liquid Metal Solutions

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Electronic Supporting Information:

Coke formation during propane dehydrogenation over Ga-Rh Supported Catalytically Active Liquid Metal Solutions

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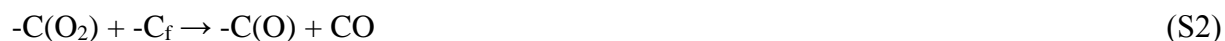
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Supplementary information

Description of coke functionalities/carbon oxide complexes

Oxidation of coke by O₂ has been hypothesised to proceed via the formation of a metastable carbon oxide complexes. The mechanism may be summarised with five steps (Equations S1-S5).^[1] At first, adsorption of O₂ on the carbon surface (C_f) initiates the formation of a metastable undissociated surface oxide -C(O₂) functionality (Equation S1), which is subsequently stabilised by evolution of CO (Equation S2). Thermal decomposition of the resulting dissociated surface oxide -C(O) or the -C(O₂) complex results in the combustion products CO and CO₂, respectively (Equation S2-S4). Furthermore, the stable complex -C(O) may react with O₂ to produce CO₂, while forming another -C(O) functionality with the next carbon surface atom (Equation 5).^[2] Any formed CO molecule is expected to undergo full oxidation to CO₂ at considerable concentrations of O₂, e.g. the concentration in ambient air.



Classification of coke^[1b, 3]

Carbonaceous deposits in spent catalysts, which are analysed by means of temperature programmed oxidation (TPO), are often classified into a “soft” and “hard” coke fraction. The exclusive parameter for this classification is the oxidation temperature (e.g. the maximum of the CO₂ formation). The first peak at lower oxidation temperatures (typically below 400 °C) is attributed to the soft coke fraction. The differences in reactivity of these fractions in terms of oxidation by O₂ is typically assigned to the particular morphology. Soft coke often comprises predominantly amorphous structures, alkylated mono- and di-aromatics, and only small amounts of polyaromatics. Contrarily, hard coke has a higher degree of graphitisation, i.e. consists of mainly poly-condensed aromatic compounds. As the presence of hydrogen atoms in the carbonaceous structure increases the reactivity, soft coke often features a larger H/C ratio than hard coke. Lastly, soft coke may represent the precursor for hard coke, e.g. via graphitisation.

Determination of the activation energy and pre-exponential factor using the isoconversional method according to Starink^[4]

The linear trend line of the Arrhenius plot provides the slope m and the y-axis intersection y_0 (Equation S6). With both, the activation energy E_a and the pre-exponential factor A can be calculated according to Equations S7 and S8, respectively. The rate constant k is then calculated according to the Arrhenius equation (Equation S9).

$$y = m x + y_0 \quad (\text{S6})$$

$$E_a = \frac{m R}{1.0008} \quad (\text{S7})$$

$$A = \frac{m}{1.0008} \exp(y_0) \quad (\text{S8})$$

$$k = A \exp\left(\frac{-E_a}{R T}\right) \quad (\text{S9})$$

Preparation of Rh/Al₂O₃ catalyst

Rh(NO₃)₃ (with a nominal Rh concentration of 1 mg L⁻¹) were added. The water was evaporated under vacuum (1 mbar) at 50 °C. The resulting off-white powder was calcined for 12 h at 450 °C. The obtained off-white material was transferred to the reduction reactor and reduced with a stream of pure H₂ (60 mL min⁻¹), at 300 °C for 3 h. The resulting grey powder was analysed by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Supplementary graphs

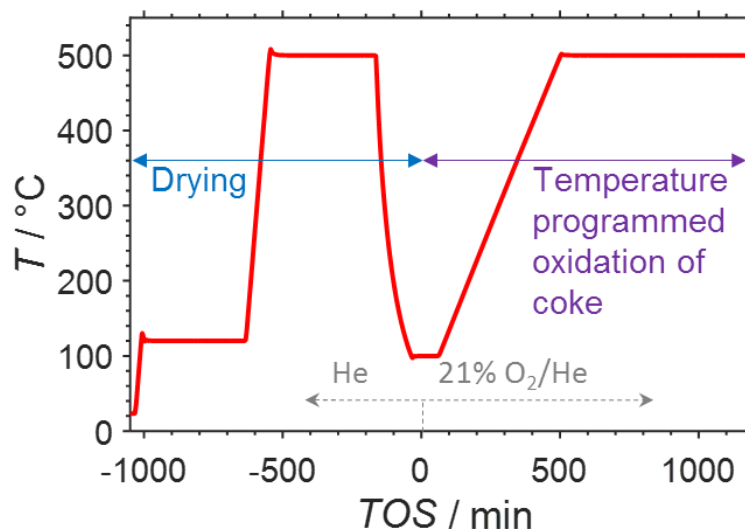


Figure S1: Experimental procedure during high-resolution thermogravimetry coupled with mass spectrometry using a XEMIS sorption analyser.

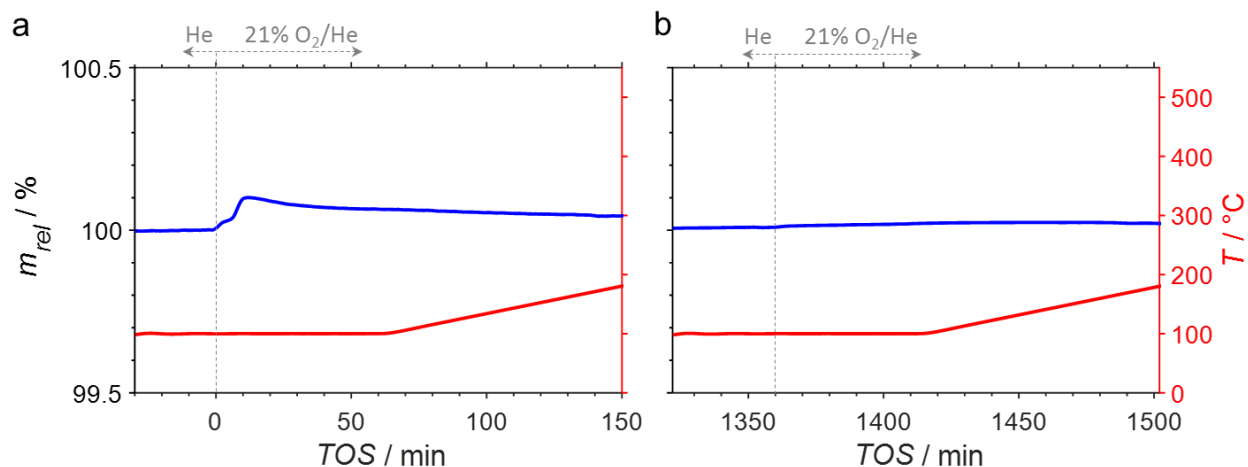


Figure S2: Sample weight relative to the weight prior to exposure to 21% O₂/He at 100 °C during the initial isotherm of (a) the first and (b) the second consecutive temperature programmed oxidation (1 °C min⁻¹) sequence of as-prepared SCALMS with an atomic Ga/Rh ratio of 125 as monitored via high-resolution thermogravimetry coupled with mass spectrometry. Conditions of the experiment: He flow 100 mL_N min⁻¹ for TOS < 0; He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS > 0; GHSV 30000 mL_N g⁻¹ h⁻¹.

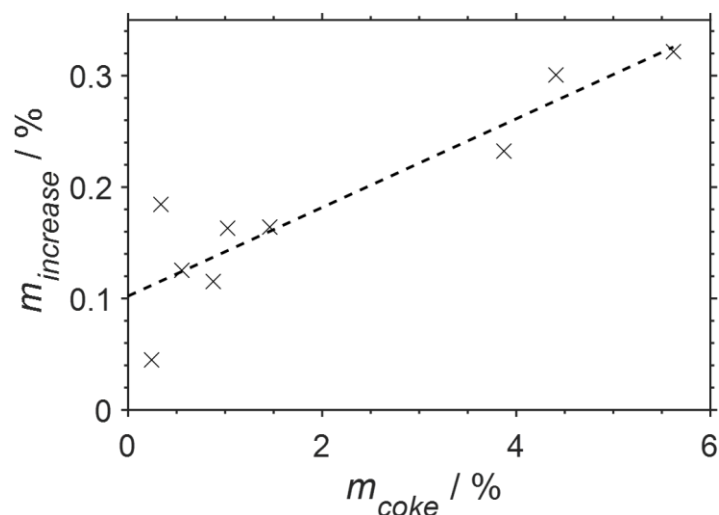


Figure S3: Dependence of the initial weight increase and the identified amount of coke during temperature programmed oxidation ($1 \text{ }^\circ\text{C min}^{-1}$) of spent SCALMS, a spent $\text{Ga}/\text{Al}_2\text{O}_3$ ($\text{Ga}/\text{Rh} = \infty$), as well as a spent $\text{Rh}/\text{Al}_2\text{O}_3$ ($\text{Ga}/\text{Rh} = 0$) reference catalyst as monitored via high-resolution thermogravimetry coupled with mass spectrometry. All catalysts were previously applied in propane dehydrogenation at $450\text{-}550 \text{ }^\circ\text{C}$.

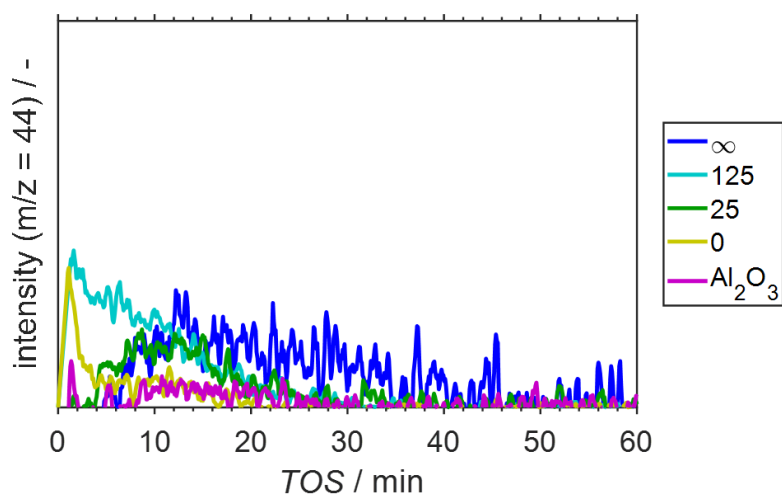


Figure S4: Formation of CO_2 during the isotherm at $100 \text{ }^\circ\text{C}$ upon first exposure to oxygen during temperature programmed oxidation of spent SCALMS with atomic Ga/Rh ratios of 25 and 125, the spent $\text{Ga}/\text{Al}_2\text{O}_3$ ($\text{Ga}/\text{Rh} = \infty$) and $\text{Rh}/\text{Al}_2\text{O}_3$ ($\text{Ga}/\text{Rh} = 0$) reference catalysts, as well as the bare Al_2O_3 support material as monitored via high-resolution thermogravimetry coupled with mass spectrometry. All catalysts were previously applied in propane dehydrogenation at $450 \text{ }^\circ\text{C}$. Conditions of the experiment: He flow $100 \text{ mL}_\text{N} \text{ min}^{-1}$ for $\text{TOS} < 0$; He flow $79 \text{ mL}_\text{N} \text{ min}^{-1}$ and O_2 flow $21 \text{ mL}_\text{N} \text{ min}^{-1}$ for $\text{TOS} > 0$; GHSV $30000 \text{ mL}_\text{N} \text{ g}^{-1} \text{ h}^{-1}$.

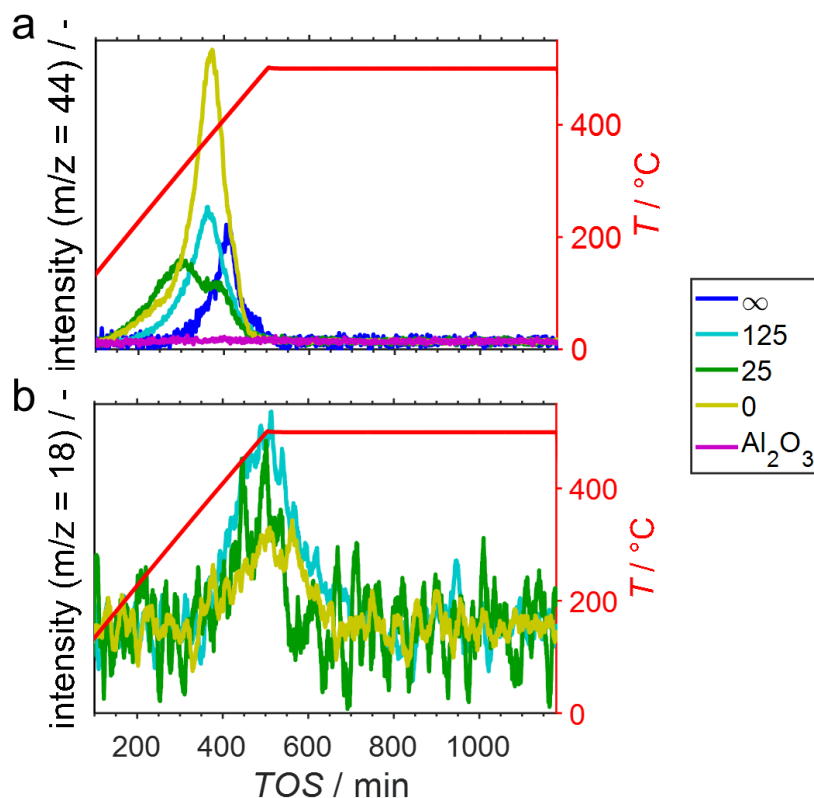


Figure S5: Formation of (a) CO₂ and (b) H₂O during temperature programmed oxidation (1 °C min⁻¹) of spent SCALMS with atomic Ga/Rh ratios of 25 and 125, the spent Ga/Al₂O₃ (Ga/Rh = ∞) and Rh/Al₂O₃ (Ga/Rh = 0) reference catalysts, as well as the bare Al₂O₃ support material as monitored via high-resolution thermogravimetry coupled with mass spectrometry. All catalysts were previously applied in propane dehydrogenation at 450 °C. Conditions of the experiment: He flow 100 mL_N min⁻¹ for TOS<0; He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS>0; GHSV 30000 mL_N g⁻¹ h⁻¹.

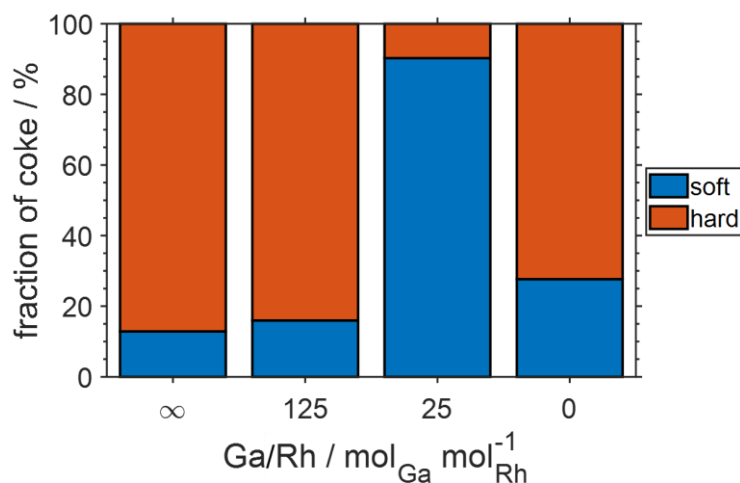


Figure S6: Identified fractions of soft and hard coke in the spent SCALMS with atomic Ga/Rh ratios of 25 and 125, as well as the spent Ga/Al₂O₃ (Ga/Rh = ∞) and Rh/Al₂O₃ (Ga/Rh = 0) reference catalysts. All catalysts were previously applied in propane dehydrogenation at 450 °C.

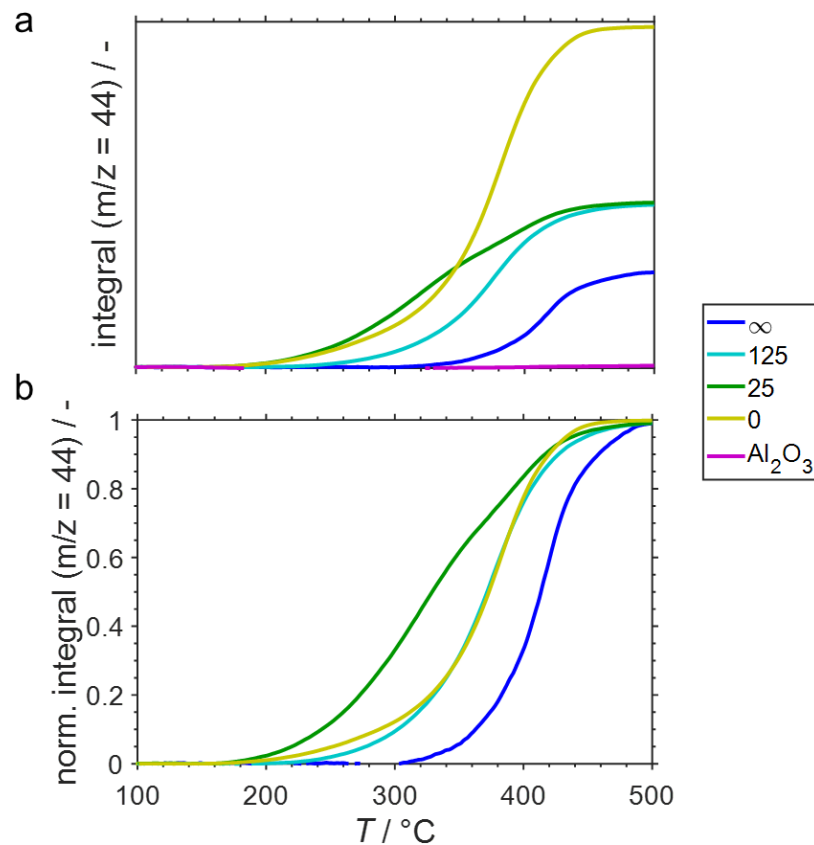


Figure S7: (a) Cumulative and (b) normalised cumulative formation of CO₂ during temperature programmed oxidation (1 °C min⁻¹) of spent SCALMS with atomic Ga/Rh ratios of 25 and 125, the spent Ga/Al₂O₃ (Ga/Rh = ∞) and Rh/Al₂O₃ (Ga/Rh = 0) reference catalysts, as well as the bare Al₂O₃ support material as monitored via high-resolution thermogravimetry coupled with mass spectrometry. All catalysts were previously applied in propane dehydrogenation at 450 °C. Conditions of the experiment: He flow 100 mL_N min⁻¹ for TOS<0; He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS>0; GHSV 30000 mL_N g⁻¹ h⁻¹.

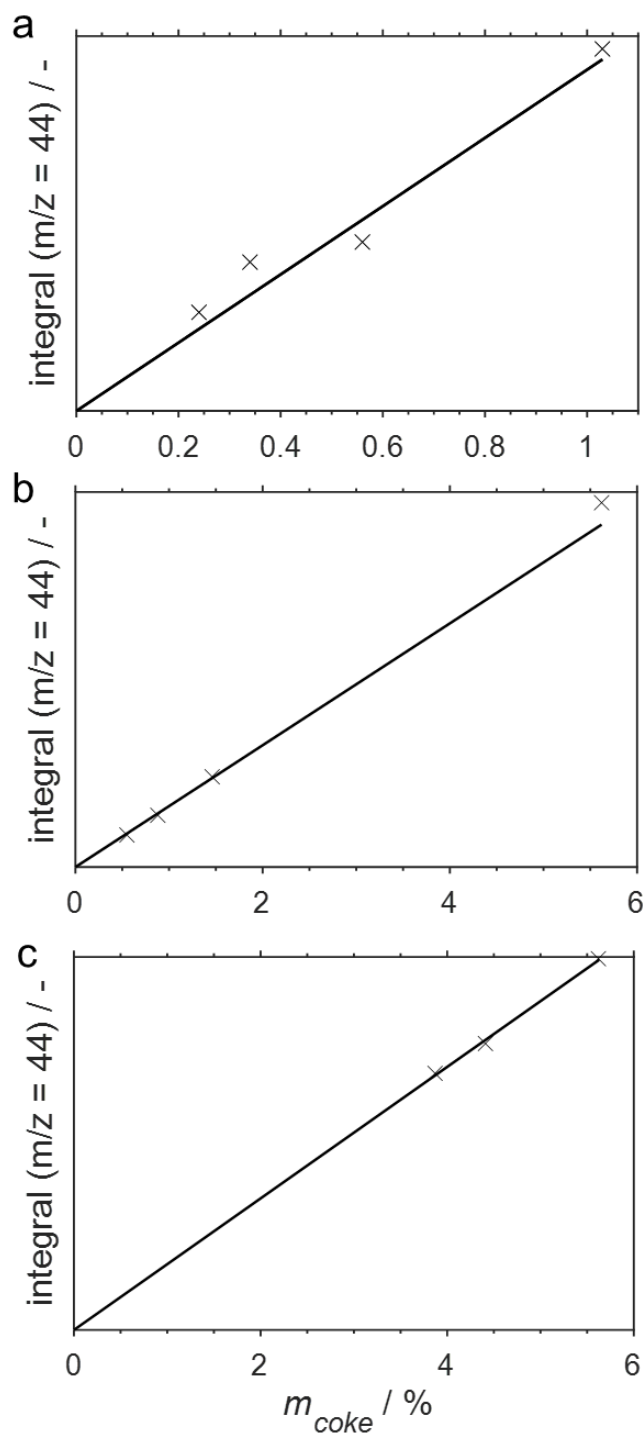


Figure S8: Parity plots of the identified amount of coke and the cumulative formation of CO_2 during temperature programmed oxidation ($1 \text{ }^\circ\text{C min}^{-1}$) of (a) spent SCALMS with atomic Ga/Rh ratios of 25 and 125, as well as the spent Ga/Al₂O₃ (Ga/Rh = ∞) and Rh/Al₂O₃ (Ga/Rh = 0) reference catalysts after application in propane dehydrogenation at 450 $^\circ\text{C}$, (b) spent SCALMS with an atomic Ga/Rh ratio 125 after propane dehydrogenation at 450, 480, 500, and 550 $^\circ\text{C}$, and (c) spent SCALMS with various atomic Ga/Rh ratios after propane dehydrogenation at 550 $^\circ\text{C}$ as monitored via high-resolution thermogravimetry coupled with mass spectrometry.

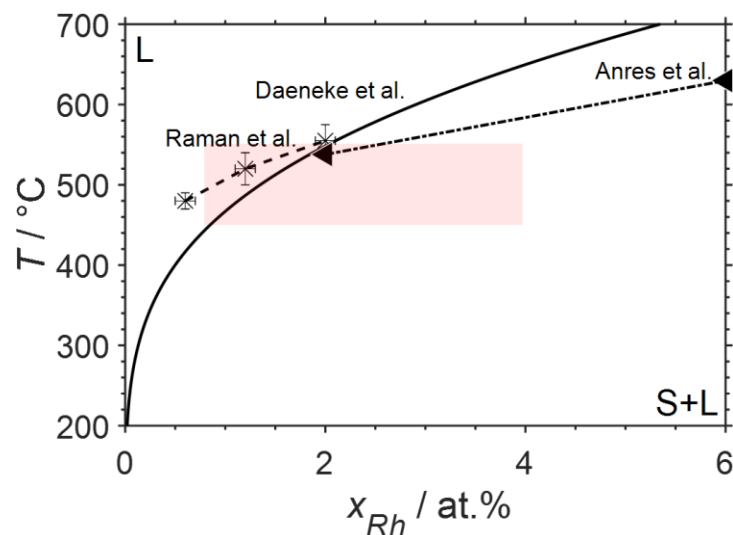


Figure S9: Studied domain for propane dehydrogenation using various compositions of SCALMS (red rectangle) superimposed on the liquidus line of the Ga-Rh phase diagram (solid) according to ref. [5], two experimental data points for the solubility of Rh in Ga (triangle connected by dash-dotted line to guide the eye) according to ref. [6], as well as an experimentally obtained solubility data from XPS measurements (crosses connected by dashed line to guide the eye) according to ref. [7].

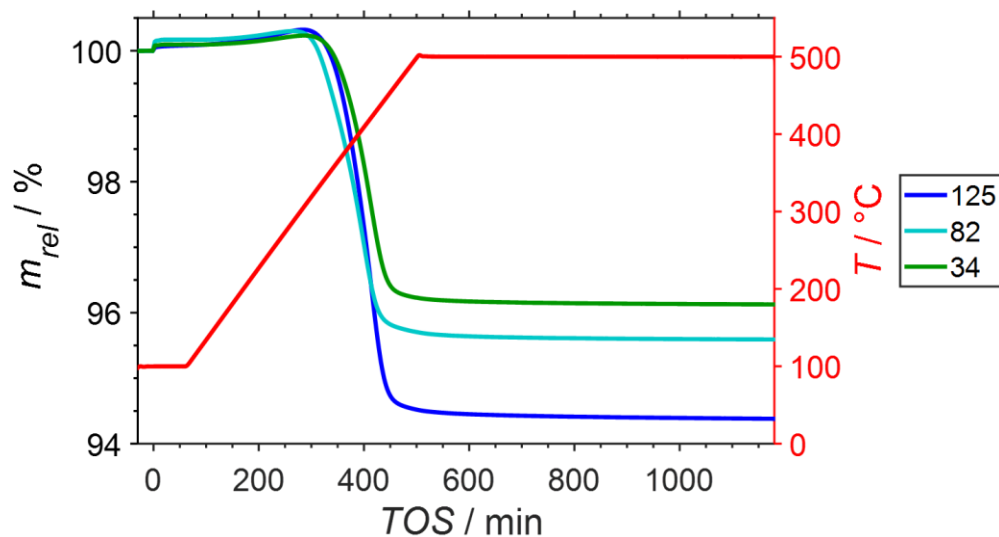


Figure S10: Sample weight relative to the weight prior to exposure to 21% O_2/He at 100 $^\circ\text{C}$ during temperature programmed oxidation (1°C min^{-1}) of spent SCALMS with various atomic Ga/Rh ratios as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The catalysts were previously applied in propane dehydrogenation at 550 $^\circ\text{C}$. Conditions of the experiment: He flow $100 \text{ mL}_\text{N} \text{ min}^{-1}$ for $\text{TOS} < 0$; He flow $79 \text{ mL}_\text{N} \text{ min}^{-1}$ and O_2 flow $21 \text{ mL}_\text{N} \text{ min}^{-1}$ for $\text{TOS} > 0$; GHSV $30000 \text{ mL}_\text{N} \text{ g}^{-1} \text{ h}^{-1}$.

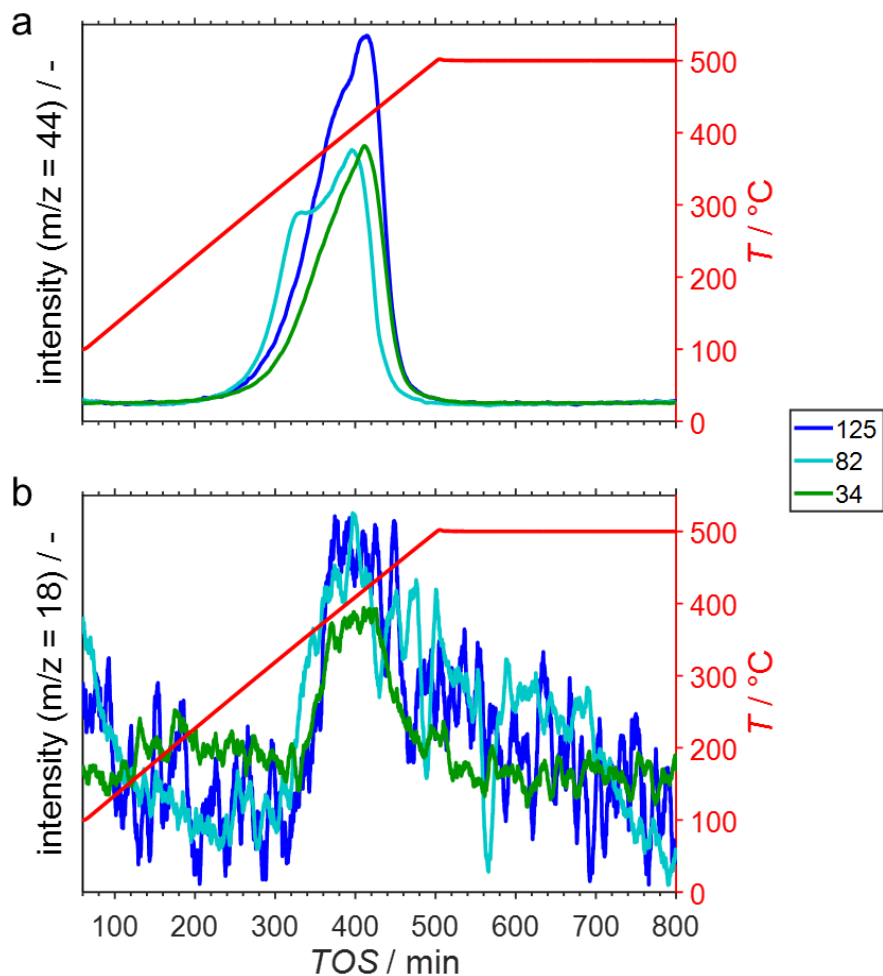


Figure S11: Formation of (a) CO_2 and (b) H_2O during temperature programmed oxidation ($1\text{ }^\circ\text{C min}^{-1}$) of spent SCALMS with various atomic Ga/Rh ratios as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The catalysts were previously applied in propane dehydrogenation at $550\text{ }^\circ\text{C}$. Conditions of the experiment: He flow $100\text{ mL}_\text{N min}^{-1}$ for $\text{TOS} < 0$; He flow $79\text{ mL}_\text{N min}^{-1}$ and O_2 flow $21\text{ mL}_\text{N min}^{-1}$ for $\text{TOS} > 0$; GHSV $30000\text{ mL}_\text{N g}^{-1}\text{ h}^{-1}$.

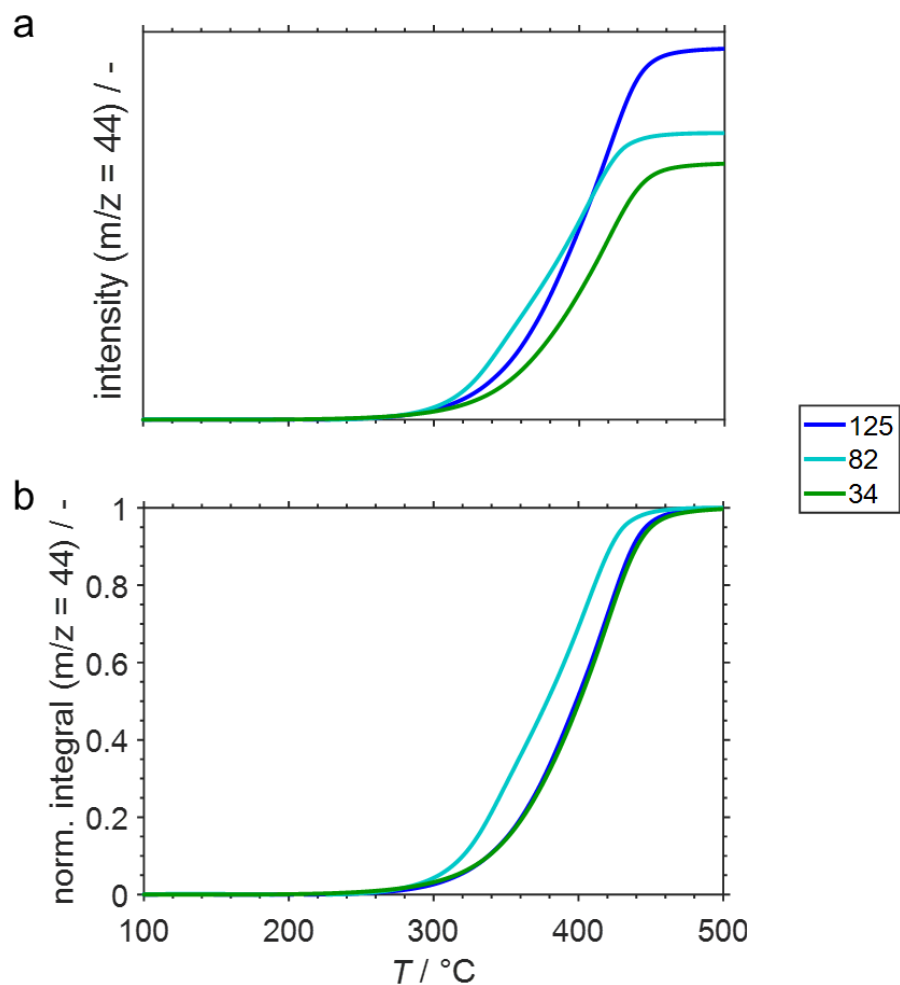


Figure S12: (a) Cumulative and (b) normalised cumulative formation of CO_2 during temperature programmed oxidation ($1\text{ }^\circ\text{C min}^{-1}$) of spent SCALMS with various atomic Ga/Rh ratios as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The catalysts were previously applied in propane dehydrogenation at $550\text{ }^\circ\text{C}$. Conditions of the experiment: He flow $100\text{ mL}_N\text{ min}^{-1}$ for $\text{TOS}<0$; He flow $79\text{ mL}_N\text{ min}^{-1}$ and O_2 flow $21\text{ mL}_N\text{ min}^{-1}$ for $\text{TOS}>0$; GHSV $30000\text{ mL}_N\text{ g}^{-1}\text{ h}^{-1}$.

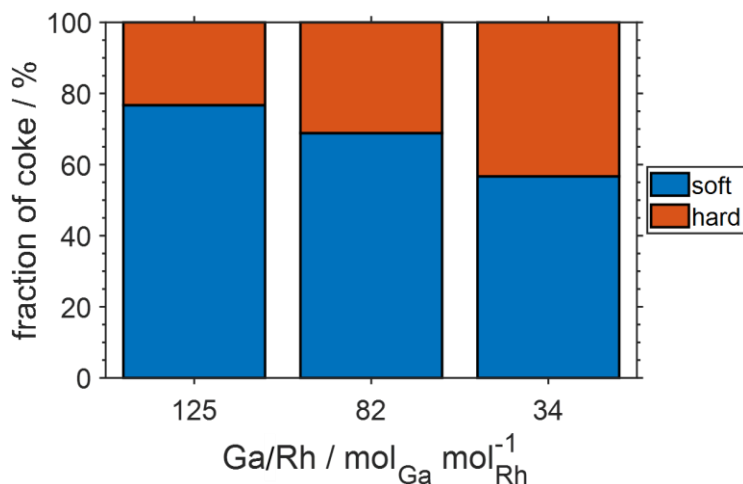


Figure S13: Identified fractions of soft and hard coke in the spent SCALMS with various atomic Ga/Rh ratios after propane dehydrogenation at 550 °C.

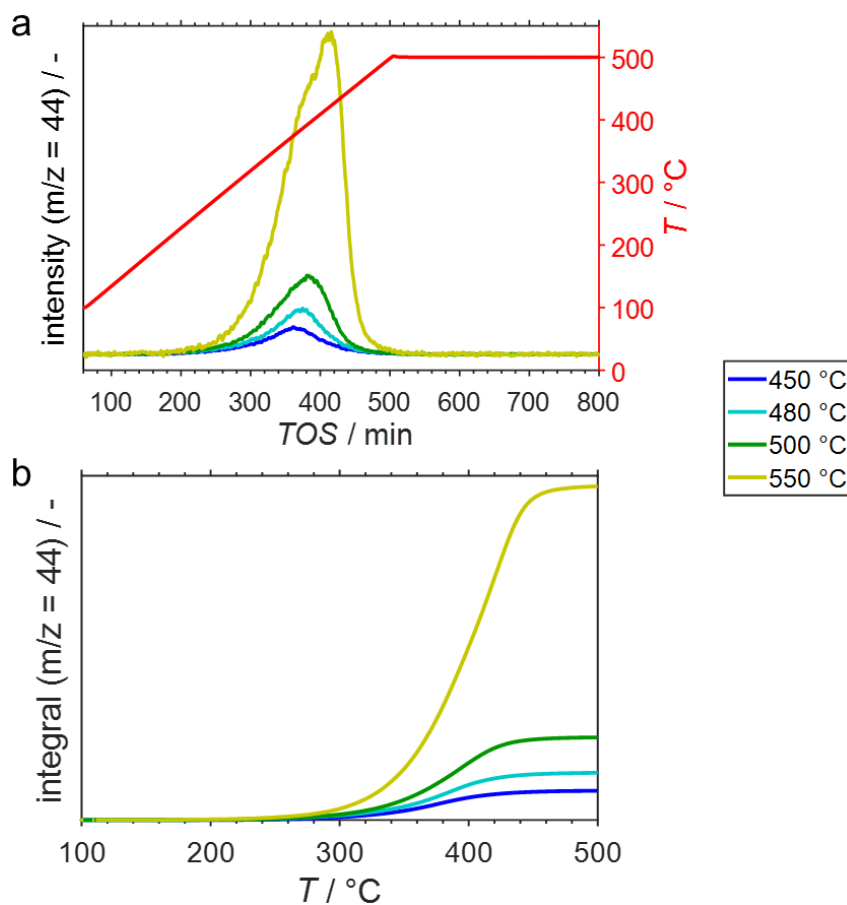


Figure S14: (a) Formation of CO₂ and (b) cumulative formation of CO₂ during temperature programmed oxidation (1 °C min⁻¹) of spent SCALMS with an atomic Ga/Rh ratio of 125 as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The catalysts were previously applied in propane dehydrogenation at 450, 480, 500, and 550 °C. Conditions of the experiment: He flow 100 mL_N min⁻¹ for TOS < 0; He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS > 0; GHSV 30000 mL_N g⁻¹ h⁻¹.

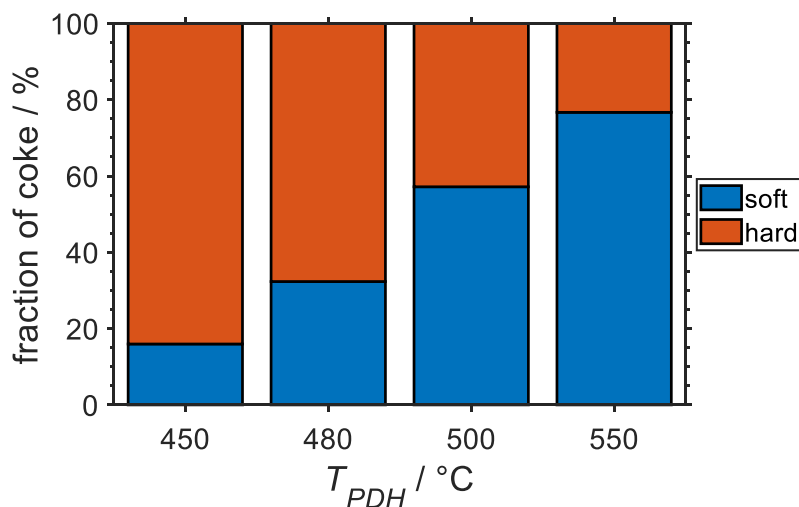


Figure S15: Identified fractions of soft and hard coke in the spent SCALMS with an atomic Ga/Rh ratio of 125 after propane dehydrogenation at 450, 480, 500, and 550 °C.

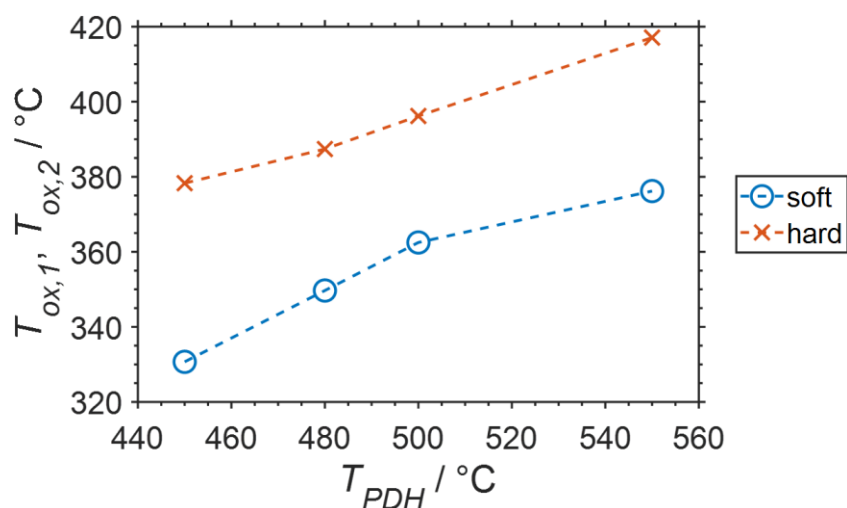


Figure S16: Peak positions of the deconvoluted contribution of soft and hard coke to the overall formation of CO_2 during temperature programmed oxidation of spent SCALMS with an atomic Ga/Rh ratio of 125 after propane dehydrogenation at 450, 480, 500, and 550 °C as monitored via high-resolution thermogravimetry coupled with mass spectrometry.

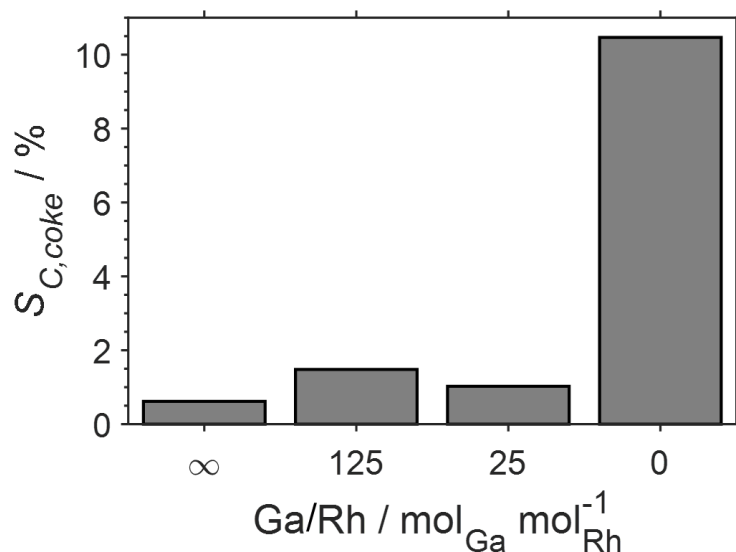


Figure S17: Integral carbon based selectivity towards coke during propane dehydrogenation at 450 °C of the SCALMS with atomic Ga/Rh ratios of 25 and 125, as well as the spent Ga/Al₂O₃ (Ga/Rh = ∞) and Rh/Al₂O₃ (Ga/Rh = 0) reference catalysts.

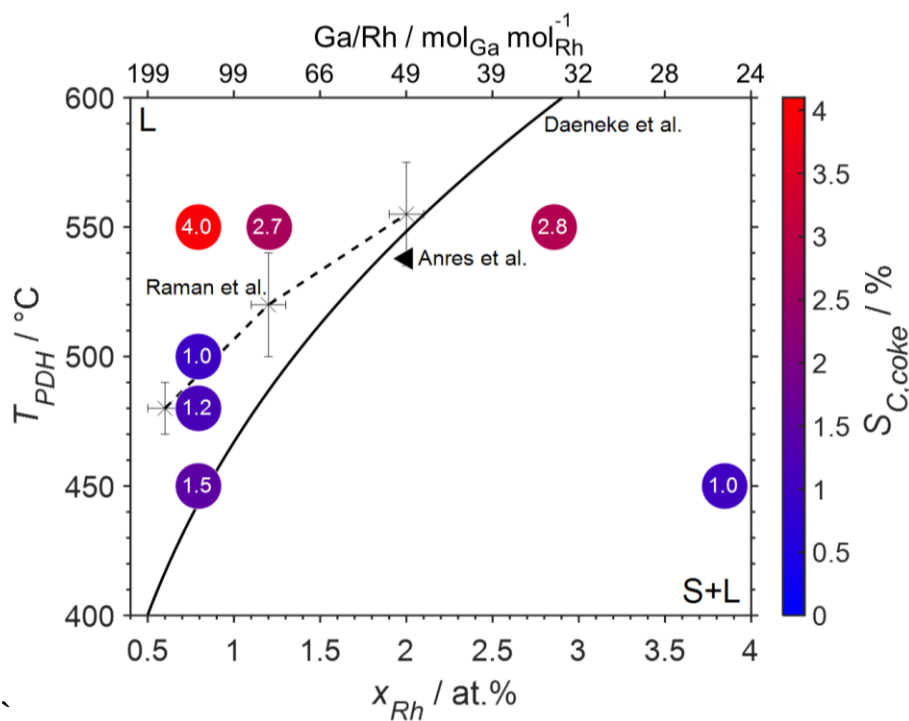


Figure S18: Integral carbon based selectivity towards coke (circles) of the various Ga-Rh SCALMS compositions at different temperatures superimposed on the liquidus line of the Ga-Rh phase diagram (solid) according to ref. [5], an experimental data point for the solubility of Rh in Ga (filled triangle) according to ref. [6], as well as an experimentally obtained solubility data from XPS measurements (crosses connected by dashed line to guide the eye) according to ref. [7].

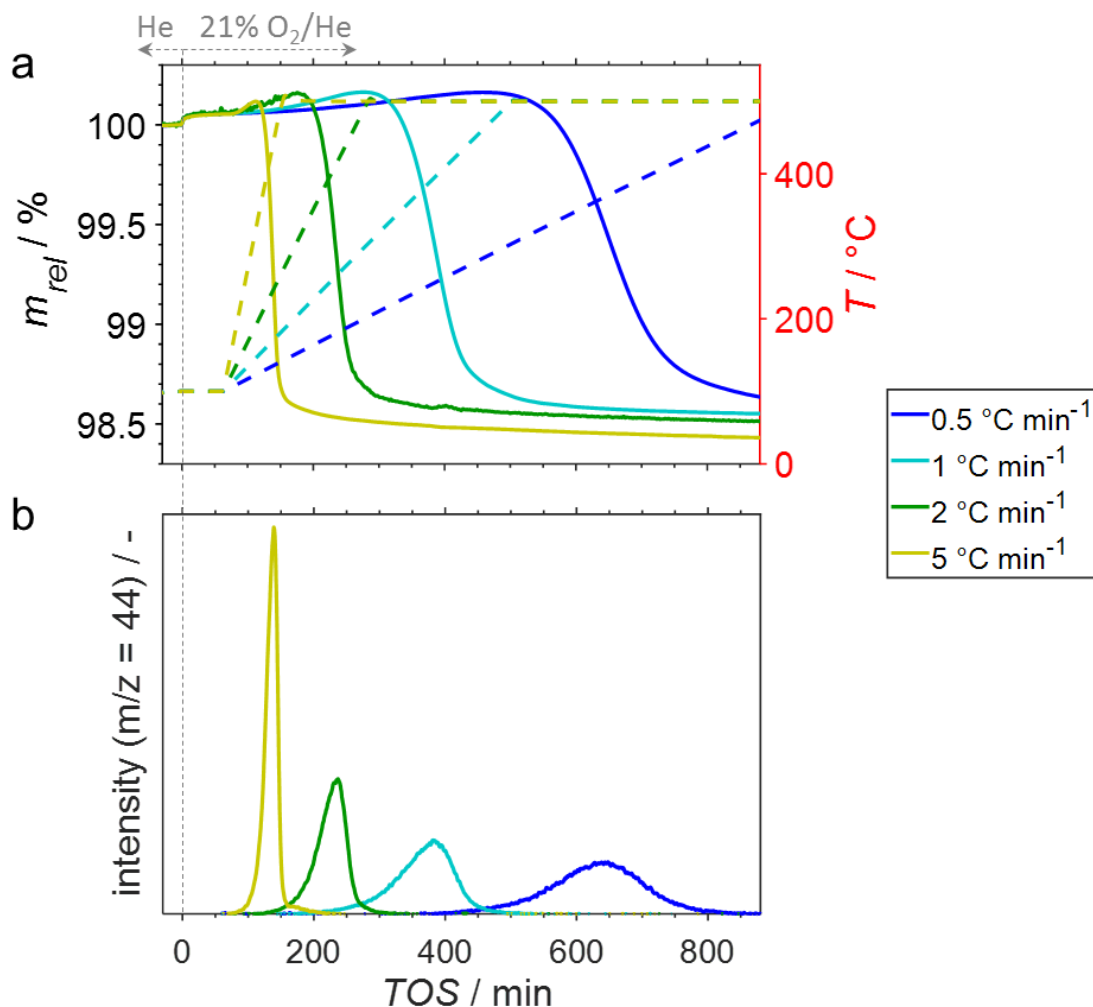


Figure S19: (a) Sample weight relative to the weight prior to exposure to 21% O₂/He at 100 °C and (b) formation of CO₂ during temperature programmed oxidation of spent SCALMS with an atomic Ga/Rh ratio of 125 at heating rates of 0.5, 1, 2, and 5 °C min⁻¹ as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The catalysts were previously applied in propane dehydrogenation at 500 °C. Conditions of the experiment: He flow 100 mL_N min⁻¹ for TOS < 0; He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS > 0; GHSV 30000 mL_N g⁻¹ h⁻¹.

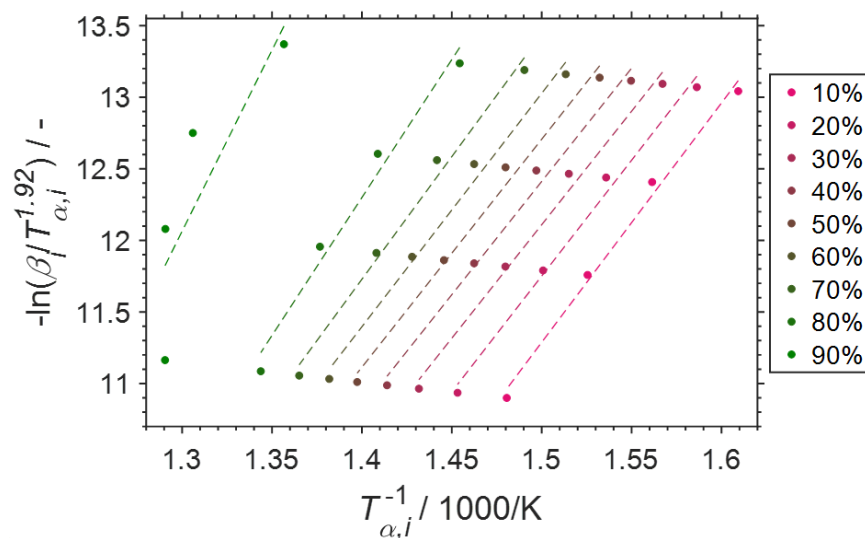


Figure S20: Isoconversional analysis in the Arrhenius plot according to Starink^[4] of various conversion levels of coke (α , filled circles) with linear trendlines (dashed) as monitored by the weight change using high-resolution thermogravimetry during temperature programmed oxidation in 21% O₂/He at different heating rates (β) for a spent SCALMS with an atomic Ga/Rh ratio of 125. The catalyst was previously applied in propane dehydrogenation at 500 °C.

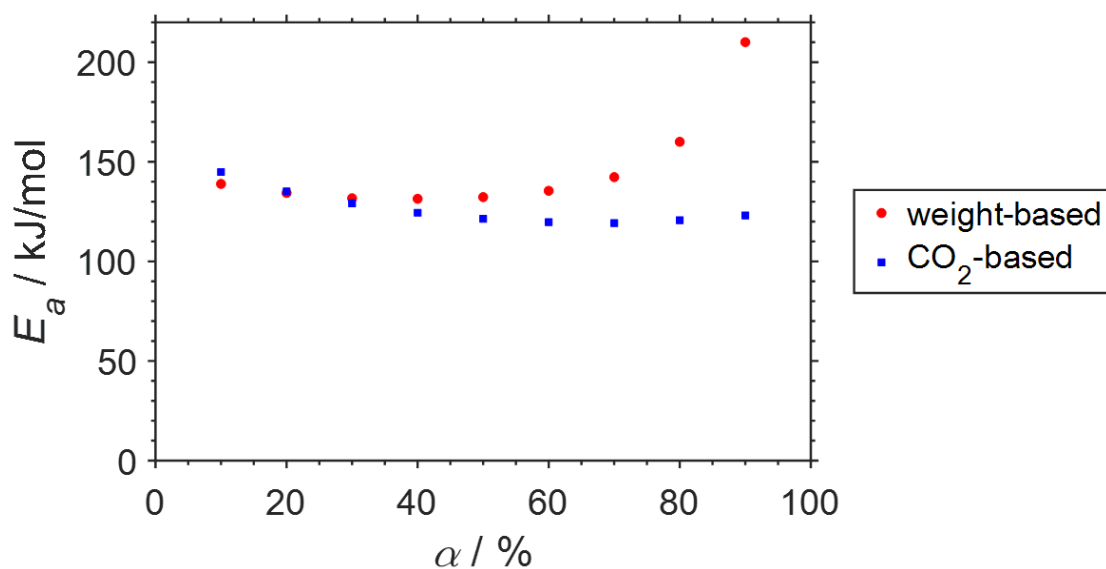


Figure S21: Comparison of the activation energies (E_a) at various conversion levels of coke (α) as derived from the Arrhenius plot based on the weight change or the formation of CO₂ during temperature programmed oxidation in 21% O₂/He of a spent SCALMS with an atomic Ga/Rh ratio of 125 as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The analysis is based on the isoconversional method by Starink^[4] and the catalyst was previously applied in propane dehydrogenation at 500 °C.

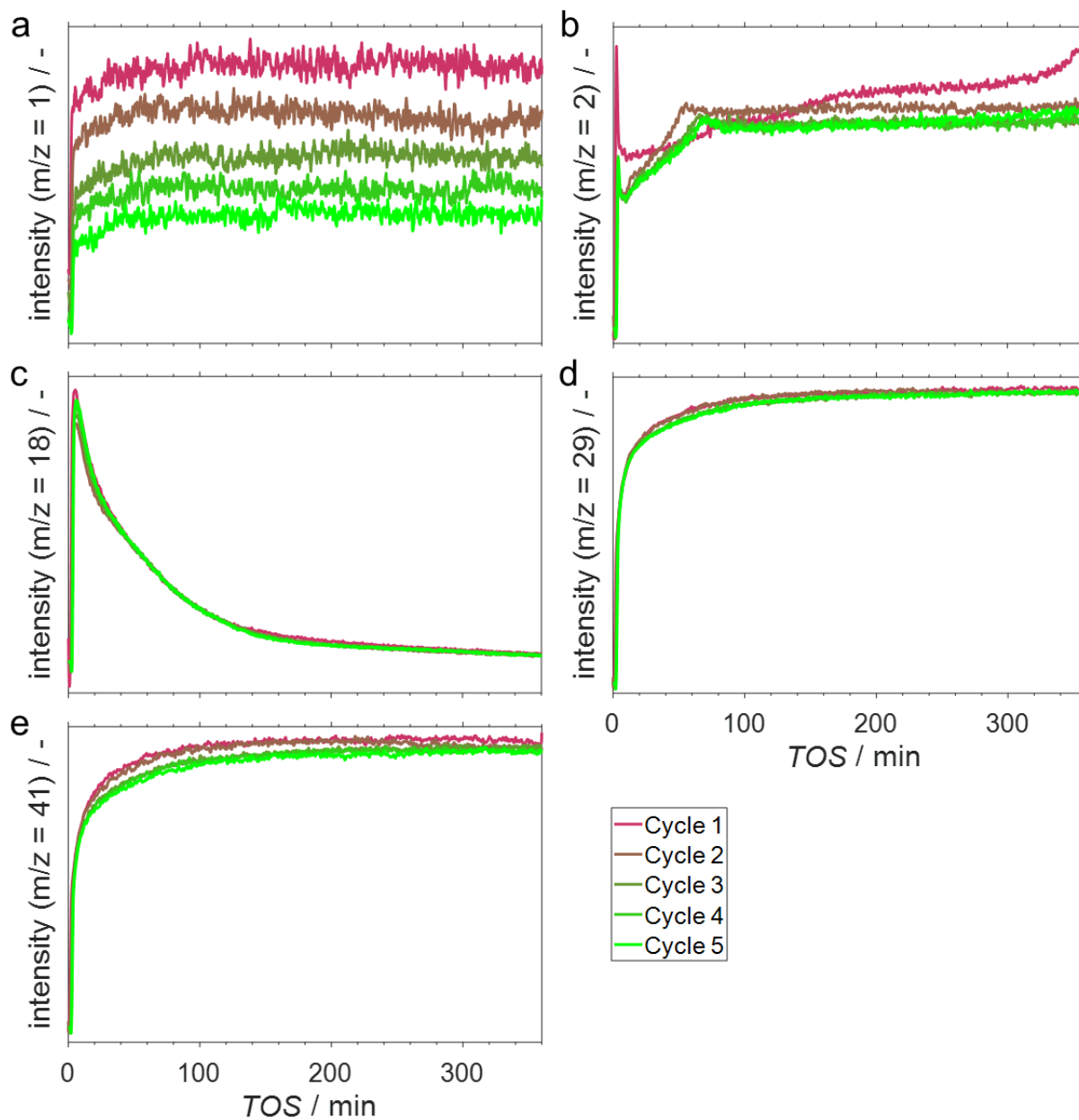


Figure S22: Selected mass-to-charge ratios representing (a) almost exclusively propene, (b) almost exclusively H_2 (c) exclusively H_2O , (d) exclusively propane, (e) combined propane and propene during the dehydrogenation cycles at $500\text{ }^\circ\text{C}$ as monitored via with mass spectrometry. Conditions of the experiment: He flow $80\text{ mL}_\text{N}\text{ min}^{-1}$ and C_3H_8 flow $20\text{ mL}_\text{N}\text{ min}^{-1}$; GHSV $30000\text{ mL}_\text{N}\text{ g}^{-1}\text{ h}^{-1}$.

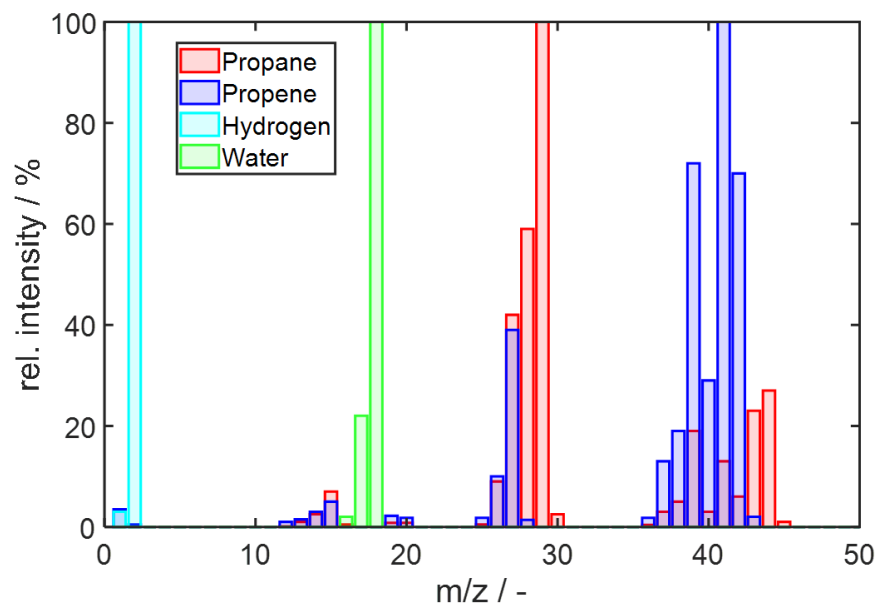


Figure S23: Mass spectra according to NIST^[8] of molecules of interest for propane dehydrogenation over SCALMS.

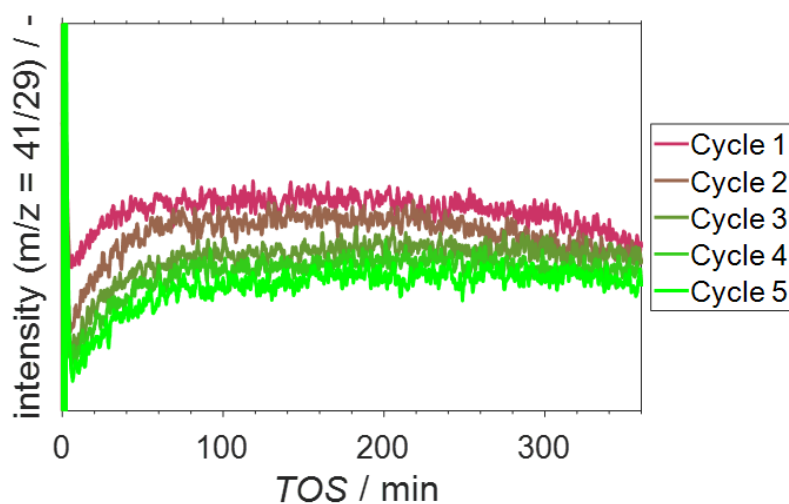


Figure S24: Mass-to-charge ratio of 41 combining propane and propene over 29 representing exclusively propane during the dehydrogenation cycles at 500 °C as monitored via mass spectrometry. Conditions of the experiment: He flow 80 mL_N min⁻¹ and C₃H₈ flow 20 mL_N min⁻¹; GHSV 30000 mL_N g⁻¹ h⁻¹.

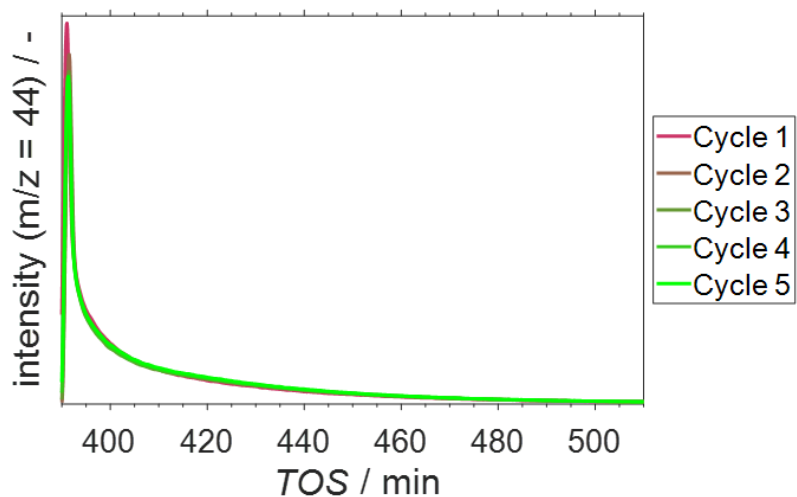


Figure S25: Formation of CO_2 during 5 cyclic regenerations at 500 °C upon propane dehydrogenation using a SCALMS with an atomic Ga/Rh ratio of 125 as monitored via with mass spectrometry. Conditions of the experiment: He flow $79 \text{ mL}_N \text{ min}^{-1}$ and O_2 flow $21 \text{ mL}_N \text{ min}^{-1}$ for $\text{TOS} > 390 \text{ min}$; GHSV $30000 \text{ mL}_N \text{ g}^{-1} \text{ h}^{-1}$.

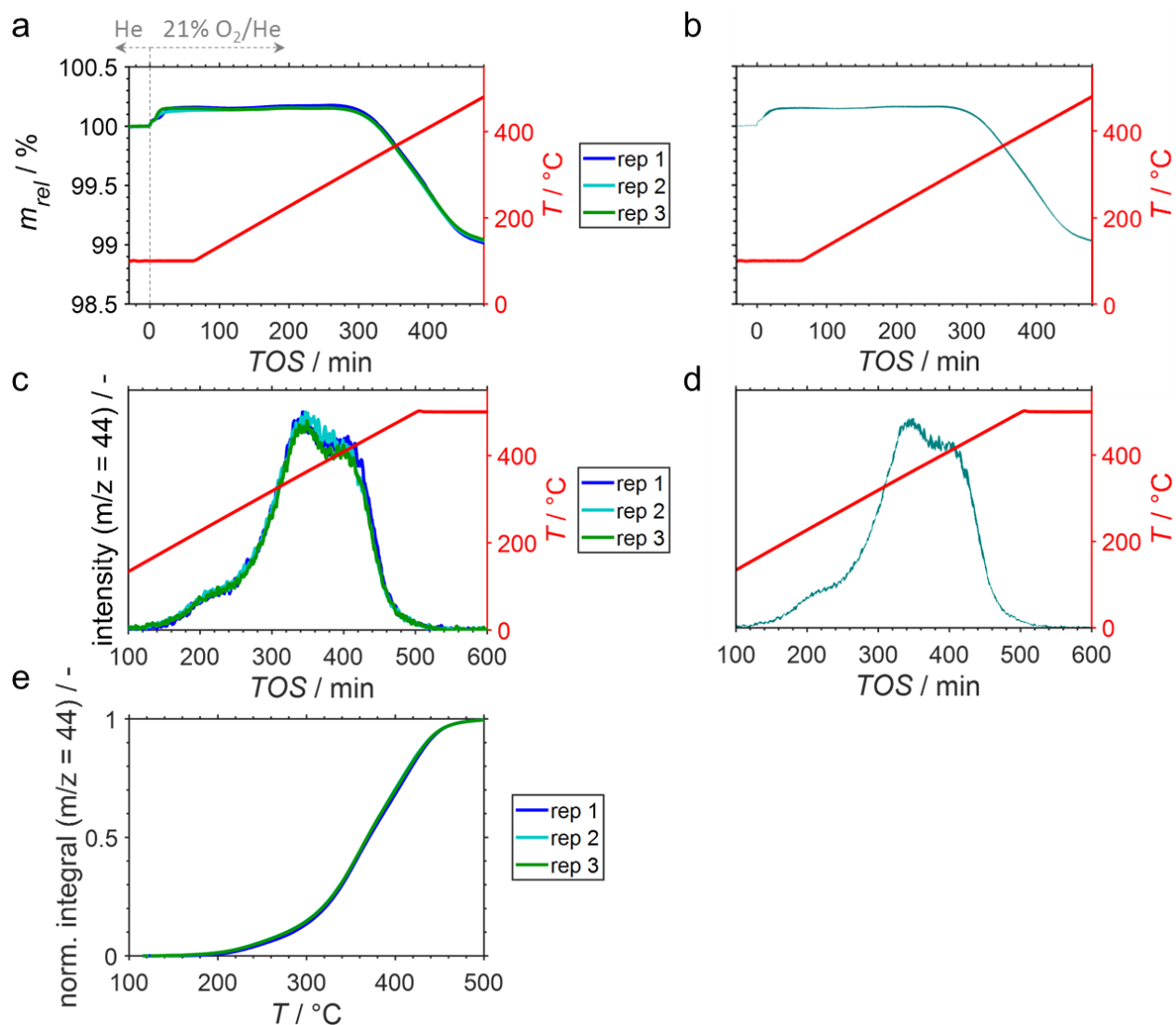


Figure S26: (a) Sample weight relative to the weight prior to exposure to 21% O₂/He at 100 °C and (c) formation of CO₂ with (b,d) the corresponding confidence intervals during reproducibility studies (three repetitions) of temperature programmed oxidation (1 °C min⁻¹) of the same spent SCALMS as monitored via high-resolution thermogravimetry coupled with mass spectrometry. The selected confidence level was 95%. Conditions of the experiment: He flow 79 mL_N min⁻¹ and O₂ flow 21 mL_N min⁻¹ for TOS > 390 min; GHSV 30000 mL_N g⁻¹ h⁻¹.

Supplementary tables

Table S1: Elemental compositions of characterised and applied SCALMS, as well as of the Ga/Al₂O₃ and Rh/Al₂O₃ reference samples.

Atomic Ga/Rh ratio	Ga / wt%	Rh / wt%
0	0	0.19
25	5.65	0.33
34	5.90	0.26
82	5.90	0.11
125	5.94	0.07
∞		0

Table S2: Characteristic temperatures during temperature programmed oxidation of spent SCALMS by means of high-resolution thermogravimetric analysis coupled with mass spectrometry (HRTGA-MS).

Catalyst	PDH temperature	T_{on}	T_{ox}	$T_{ox,1}$	$T_{ox,2}$	T_{50}
Ga/Rh = 0	450	344	382	344	384	386
Ga/Rh = 25	450	282	331	320	407	345
Ga/Rh = 125	450	345	381	331	378	384
Ga/ Rh = ∞	450	390	419	376	417	421
Ga/Rh = 125	480	351	389	350	387	388
Ga/Rh = 125	500	356	399	363	396	393
Ga/Rh = 125	550	370	423	387	424	399
Ga/Rh = 34	550	373	420	371	415	401
Ga/Rh = 82	550	348	406	336	395	378

Where the temperature with the greatest slope corresponds to the temperature of maximum oxidation rate (T_{ox}), i.e. the maximum weight loss. The extrapolated onset temperature of coke oxidation (T_{on}) is the point of intersection of the tangent at T_{ox} with the maximum weight during TPO.^[9] The maximum of the two peaks after deconvolution defines the alternative temperatures of maximum oxidation ($T_{ox,1}$, $T_{ox,2}$) based on formation of CO₂. The temperature at which 50% of coke are oxidised (T_{50}) is determined via cumulative integration of the MS signals.

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