Supporting Information for:

Application of modulation excitation-phase sensitive detection-DRIFTS for in situ/operando characterization of heterogeneous catalysts

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Figure S1. Residence time distribution simulation of two CSTR reactors in series by inducing a sine waveform with a periodic concentration change in the feed with periods of: A) 90 s, B) 30 s, and C) 10 s. First reactor simulates a small void-volume reaction cell (τ1 = 1 s) and the second simulates the mass spectrometer mixing chamber. Concentration exiting CSTR #1 = orange, solid line; concentration exiting CSTR #2 = black, dotted line. Conditions: (CSTR #1 average residence time) τ1 = 1 s; (CSTR #2 average residence time) τ2 = 1 s; (feed modulation low relative concentration) C low/Co = 0; (feed modulation high relative concentration) C high/Co = 1.
Figure S2. Residence time distribution simulation of two CSTR reactors in series by inducing a sine waveform with a periodic concentration change in the feed with periods of: A) 90 s, B) 30 s, and C) 10 s. First reactor simulates a large void-volume reaction cell ($\tau_1 = 25$ s) and the second simulates the mass spectrometer mixing chamber. Concentration exiting CSTR #1 = orange, solid line; concentration exiting CSTR #2 = black, dotted line. Conditions: (CSTR #1 average residence time) $\tau_1 = 25$ s; (CSTR #2 average residence time) $\tau_2 = 1$ s; (feed modulation low relative concentration) $C_{\text{low}}/C_0 = 0$; (feed modulation high relative concentration) $C_{\text{high}}/C_0 = 1$. 
Figure S3. In situ ME-PSD-DRIFTS spectra during ethanol conversion on $\gamma$-Al$_2$O$_3$. A) Time domain (TD) spectrum at 630 s; TD response at: B) 3754 cm$^{-1}$; C) 3741 cm$^{-1}$; D) 3720 cm$^{-1}$ (blue line at 630 s); FD plot at 630 s and: B') 3754 cm$^{-1}$; C') 3741 cm$^{-1}$; D') 3720 cm$^{-1}$ (red lines at $f_0$).

Conditions: 473 K, 101.3 kPa, feed modulation from He/Ar $\rightarrow$ He + EtOH (1 kPa), modulation frequency = 1/90 Hz (period = 90 s), total gas flow $\sim$40 NTP cm$^3$/min, catalyst weight $\sim$45 mg. Phase angle = (time in s/period in s)$\times$360°.
Figure S4. In situ ME-PSD-DRIFTS spectra during ethanol conversion on γ-Al_2O_3. TD response at: A) 3680 cm\(^{-1}\); B) 3208 cm\(^{-1}\); C) 2968 cm\(^{-1}\); D) 2925 cm\(^{-1}\); E) 2880 cm\(^{-1}\); F) 1388 cm\(^{-1}\) (blue line at 630 s); FD plot at 630 s and: A’) 3680 cm\(^{-1}\); B’) 3208 cm\(^{-1}\); C’) 2968 cm\(^{-1}\); D’) 2925 cm\(^{-1}\); E’) 2880 cm\(^{-1}\); F’) 1388 cm\(^{-1}\) (red lines at 1f_0); Conditions: same as in Figure S3.
Figure S5. In situ ME-PSD-DRIFTS spectra during ethanol conversion on γ-Al₂O₃. TD response at: A) 1137 cm⁻¹; B) 1063 cm⁻¹; C) 1033 cm⁻¹ (blue line at 630 s); FD plot at 630 s for: A’) 1137 cm⁻¹; B’) 1063 cm⁻¹; C’) 1033 cm⁻¹ (red lines at 1f₀); Conditions: same as in Figure S3.

Figure S6. Phase domain magnitude plot (showing all positive observed peaks) at a frequency of 0.011 Hz. Conditions: 473 K, 101.3 kPa, feed modulation from He/Ar → He + EtOH (1 kPa), modulation frequency = 1/90 Hz, total gas flow ~40 NTP cm³/min, catalyst weight ~45 mg. Phase angle = (radians/2π)×360°. A scaled gas phase EtOH IR spectrum is shown for comparison to verify absence of EtOH gas phase contributions to the phase domain spectra.
S1. Modelling of feed modulation and reaction cell frequency response in a two CSTR in series model (no reaction)

1. Fourier series for waveforms with fundamental angular frequency $\omega_0$ and bounded by $[-1, 1]$:

Square wave

$$ f(t) = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{\sin[(2k-1)\omega_0 t]}{2k-1} = \frac{2}{\pi i} \sum_{k=\infty}^{\infty} \frac{\exp[i(2k-1)\omega_0 t]}{2k-1} $$

Equation 1

2. The transformation of each component in the Fourier series ($z_n \exp(i\omega_n t)$) through two CSTRs is performed individually in the $s$-domain via Laplace transform:

$$ L\{z_n \exp(i\omega_n t)\} = \frac{z_n}{s - i\omega_n} $$

Equation 2

For a CSTR model:

$$ \tau \frac{dc_{out}}{dt} = c_{in} - c_{out} \rightarrow L[\tau s c_{out} - c_{out}(t=0)] = c_{in} - c_{out} $$

Equation 3

Its transfer function is:

$$ T_L(s) = \frac{1}{1 + \tau s} $$

Equation 4

Its initial condition is:

$$ I_L(s) = \frac{\tau f_0}{1 + \tau s} $$

Equation 5

The output components with angular frequency $\omega_n$ from the first and the second CSTRs are:

$$ F_{n,1}(s) = \frac{z_n}{s - i\omega_n} \frac{1}{1 + \tau_1 s} $$

Equation 6
\[
F_{n,2}(s) = \frac{z_n}{s - i\omega_n(1 + \tau_1 s + \tau_2 s)}
\]

Equation 7

Additional terms are generated from initial conditions:

\[
F_{\text{init},1}(s) = \frac{\tau_1 c_{\text{init},1}}{1 + \tau_1 s}
\]

Equation 8

\[
F_{\text{init},2}(s) = \frac{\tau_1 c_{\text{init},1} + \tau_2 c_{\text{init},2}}{(1 + \tau_1 s)(1 + \tau_2 s)}
\]

Equation 9

The inverse Laplace transforms of the expressions are:

\[
f_{n,1}(t) = z_n \frac{\exp(i\omega_n t) - \exp\left(-\frac{t}{\tau_1}\right)}{1 + i\omega_n \tau_1}
\]

Equation 10

\[
f_{n,2}(t) = \begin{cases} 
    z_n \left[ \frac{\exp(i\omega_n t) - \exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)}{1 + \tau_1 s} \right], & \tau_1 = \tau_2; \\
    z_n \left[ \frac{\exp(i\omega_n t)}{1 + i\omega_n \tau_1} + \frac{\exp\left(-\frac{t}{\tau_1}\right)}{(1 + \tau_1 s)(1 + \tau_2 s)} \right], & \tau_1 \neq \tau_2
\end{cases}
\]

Equation 11

\[
f_{\text{init},1}(t) = c_{\text{init},1} \exp\left(-\frac{t}{\tau_1}\right)
\]

Equation 12

\[
f_{\text{init},2}(t) = \begin{cases} 
    c_{\text{init},1} \exp\left(-\frac{t}{\tau_1}\right) + c_{\text{init},2} \exp\left(-\frac{t}{\tau_2}\right), & \tau_1 = \tau_2; \\
    \frac{c_{\text{init},1}}{\tau_1 - \tau_2} \left[ \exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right) \right] + c_{\text{init},2} \exp\left(-\frac{t}{\tau_2}\right), & \tau_1 \neq \tau_2
\end{cases}
\]

Equation 13

3. Finally, applying the last four equations to any input with the Fourier series

\[
f_{\text{in}}(t) = \sum_{n=0}^{N} z_n \exp(i\omega_n t)
\]

Equation 14
Assuming initial concentrations in the two CSTRs are $c_{init,i} \ (i = 1, 2)$, the outputs from the CSTRs are:

$$f_{out,i}(t) = f_{init,i}(t) + \sum_{n=0}^{N} f_{n,i}(t)$$

Equation 15

Note that the exponential terms with the form $\exp\left(-\frac{t}{\tau_i}\right)$ decays to negligible level after the signals are periodic. Beyond $t = 5 \max(\tau_1, \tau_2)$, the following approximations may be used [$\exp(-5) < 0.7\%$]

$$f_{n,1}(t) = \frac{\exp(i\omega_n t)}{1 + i\omega_n \tau_1}$$

Equation 16

$$f_{n,2}(t) = \frac{\exp(i\omega_n t)}{(1 + i\omega_n \tau_1)(1 + i\omega_n \tau_2)}$$

Equation 17

$$f_{init,1}(t) = f_{init,2}(t) = 0$$

Equation 18

4. The following Fourier series are used to calculate the outputs from the CSTRs after the modulation is steady.

**Square wave**

$$f_{in}(t) = \frac{2}{\pi i} \sum_{k=-\infty}^{\infty} \frac{\exp[i(2k-1)\omega_f t]}{2k-1}$$

Equation 19

$$f_1(t) = \frac{2}{\pi i} \sum_{k=-\infty}^{\infty} \frac{\exp[i(2k-1)\omega_f t]}{(2k-1)[1+i(2k-1)\omega_f \tau_1]}$$

Equation 20

$$f_2(t) = \frac{2}{\pi i} \sum_{k=-\infty}^{\infty} \frac{\exp[i(2k-1)\omega_f t]}{(2k-1)[1+i(2k-1)\omega_f \tau_1][1+i(2k-1)\omega_f \tau_2]}$$

Equation 21
Table S1. Feed modulation forms and outputs in two CSTR in series model (no reaction), CSTR1=in situ cell, CSTR2=MS

<table>
<thead>
<tr>
<th>Fourier Series Waveform</th>
<th>Initial outputs</th>
<th>Output from CSTR1</th>
<th>Output from CSTR2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sine wave</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f(t) = \sin (\omega_0 t)$</td>
<td>$f_{in}(t) = \frac{1}{2i} \left[ \exp (i\omega_0 t) - \exp (-i\omega_0 t) \right]$</td>
<td>$f_1(t) = \frac{1}{2i} \left[ \frac{\exp (i\omega_0 t)}{1 + i\omega_0 \tau_1} - \frac{\exp (-i\omega_0 t)}{1 - i\omega_0 \tau_1} \right]$</td>
<td>$f_2(t) = \frac{1}{2i} \left[ \frac{\exp (i\omega_0 t)}{(1 + i\omega_0 \tau_1)(1 + i\omega_0 \tau_2)} - \frac{\exp (-i\omega_0 t)}{(1 - i\omega_0 \tau_1)(1 - i\omega_0 \tau_2)} \right]$</td>
</tr>
<tr>
<td><strong>Cosine wave</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f(t) = \cos (\omega_0 t)$</td>
<td>$f_{in}(t) = \frac{1}{2} \left[ \exp (i\omega_0 t) + \exp (-i\omega_0 t) \right]$</td>
<td>$f_1(t) = \frac{1}{2} \left[ \frac{\exp (i\omega_0 t)}{1 + i\omega_0 \tau_1} + \frac{\exp (-i\omega_0 t)}{1 - i\omega_0 \tau_1} \right]$</td>
<td>$f_2(t) = \frac{1}{2} \left[ \frac{\exp (i\omega_0 t)}{(1 + i\omega_0 \tau_1)(1 + i\omega_0 \tau_2)} + \frac{\exp (-i\omega_0 t)}{(1 - i\omega_0 \tau_1)(1 - i\omega_0 \tau_2)} \right]$</td>
</tr>
<tr>
<td><strong>Square wave</strong></td>
<td></td>
<td></td>
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</tr>
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<td>$f(t) = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{\sin [(2k - 1)\omega_0 t]}{2k - 1}$</td>
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<td>$f_2(t) = \frac{2}{\pi i} \sum_{k=-\infty}^{\infty} \frac{\exp [i(2k - 1)\omega_0 t]}{(2k - 1)[1 + i(2k - 1)\omega_0 \tau_1][1 + i(2k - 1)\omega_0 \tau_2]}$</td>
</tr>
<tr>
<td><strong>Sawtooth wave</strong></td>
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<tr>
<td>$f(t) = \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{(-1)^{k+1} \sin (k\omega_0 t)}{k}$</td>
<td>$f_{in}(t) = \frac{1}{\pi i} \sum_{k=-\infty \neq 0}^{\infty} \frac{(-1)^{k+1} \exp (ik\omega_0 t)}{k}$</td>
<td>$f_1(t) = \frac{1}{\pi i} \sum_{k=-\infty \neq 0}^{\infty} \frac{(-1)^{k+1} \exp (ik\omega_0 t)}{k(1 + ik\omega_0 \tau_1)}$</td>
<td>$f_2(t) = \frac{1}{\pi i} \sum_{k=-\infty \neq 0}^{\infty} \frac{(-1)^{k+1} \exp (ik\omega_0 t)}{k(1 + ik\omega_0 \tau_1)(1 + ik\omega_0 \tau_2)}$</td>
</tr>
<tr>
<td><strong>Triangle wave</strong></td>
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<tr>
<td>$f(t) = \frac{8}{\pi^2} \sum_{k=1}^{\infty} \frac{(-1)^{k+1} \sin [(2k - 1)\omega_0 t]}{(2k - 1)^2}$</td>
<td>$f_{in}(t) = \frac{4}{\pi^2 i} \sum_{k=-\infty}^{\infty} \frac{(-1)^{k+1} \exp [(2k - 1)\omega_0 t]}{(2k - 1)^2}$</td>
<td>$f_1(t) = \frac{4}{\pi^2 i} \sum_{k=-\infty}^{\infty} \frac{(-1)^{k+1} \exp [(2k - 1)\omega_0 t]}{(2k - 1)^2[1 + i(2k - 1)\omega_0 \tau_1]}$</td>
<td>$f_2(t) = \frac{4}{\pi^2 i} \sum_{k=-\infty}^{\infty} \frac{(-1)^{k+1} \exp [(2k - 1)\omega_0 t]}{(2k - 1)^2[1 + i(2k - 1)\omega_0 \tau_1][1 + i(2k - 1)\omega_0 \tau_2]}$</td>
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