

## Electronic Supplementary Information (ESI) for

# Spatial activity profiling along a fixed bed of powder catalyst during selective oxidation of propylene to acrolein

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## 1. Raw data during profile acquisition

For acquisition of the profiles along the fixed-bed catalyst at an oven temperature of 400 °C (setpoint), the position with respect to the sampling orifices (*via* linear stage), the gas phase temperature at the sampling orifice (*via* inserted type-K thermocouple), the local gas phase concentration (*via* mass spectrometer (MS)) and integral catalytic performance (*via* gas chromatograph (GC)) were recorded simultaneously. Corresponding data is shown in Figure S1.

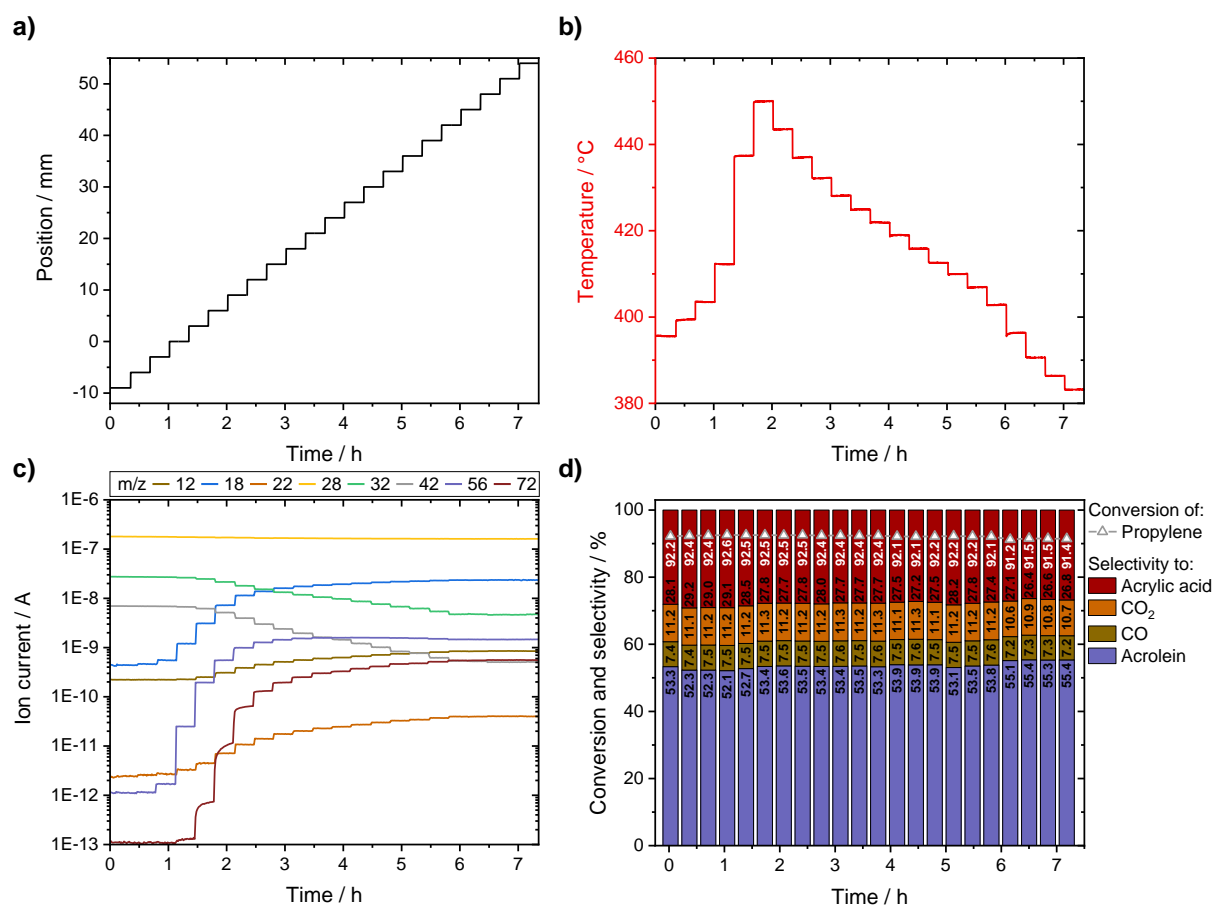


Figure S1: Obtained raw data during profile acquisition. Position along the catalyst bed (a), gas phase temperature at the sampling orifice (b), MS data representing local gas phase composition (c), and integral GC data (d).

## 2. Position and time averaged data

For the depiction of the gas phase concentration and temperature profiles, the last five minutes of temperature and ion current acquisition at each position were averaged. In the case of temperature this corresponded to the averaging of 60 individual points, resulting in the profile shown in Figure S2a. In the case of mass spectrometric data, 5-6 individual points for each m/z ratio were averaged, resulting in the profiles shown in Figure S2b. Furthermore, bypass and individual GC measurements during profile acquisition were averaged (see Figure S2c) to correlate MS with GC data for the quantification of the MS data along the catalyst bed. The averaged performance of the catalyst during profile acquisition is shown in Figure S2d.

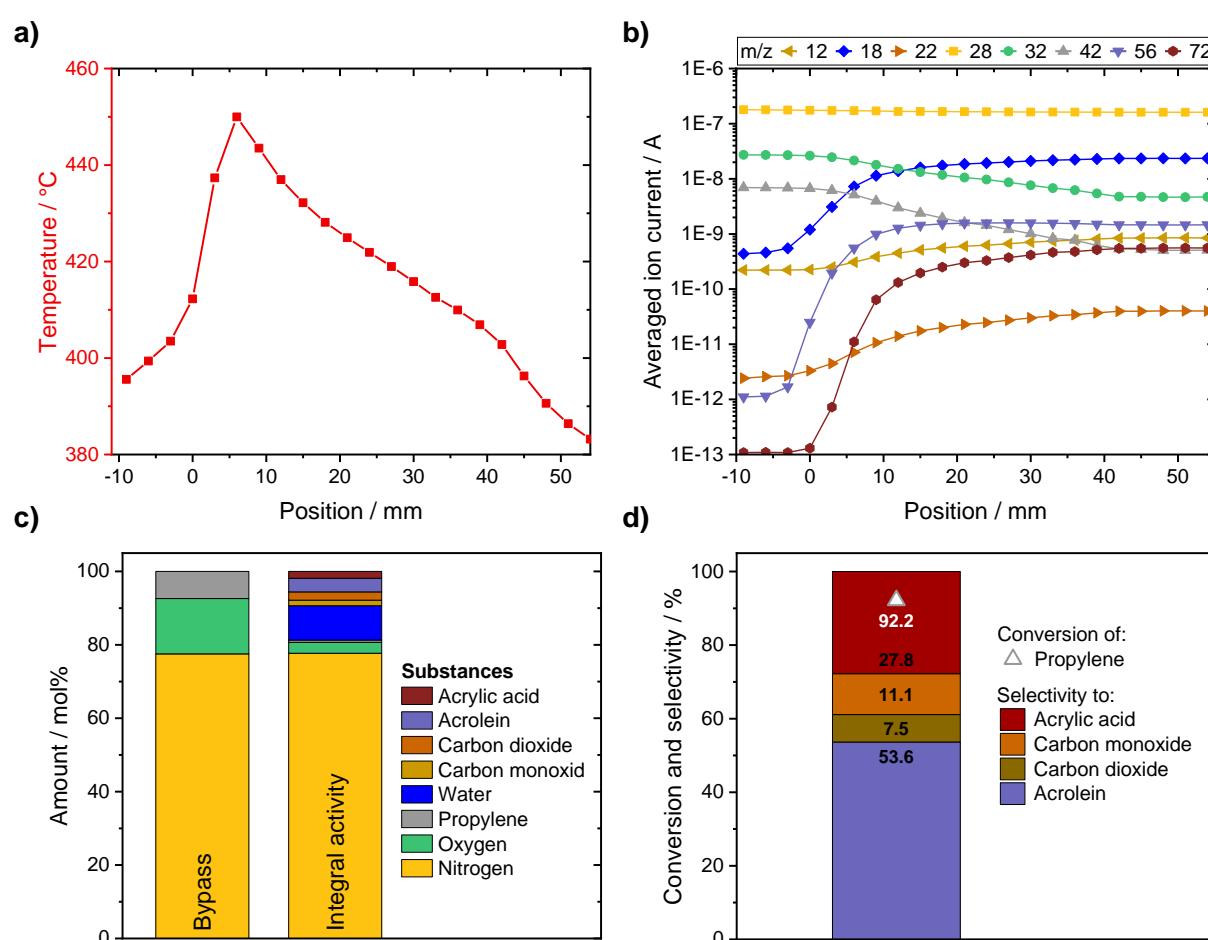


Figure S2: Spatially resolved and integral activity data during profile acquisition. Axially resolved temperature profile (a), axially resolved MS profile for selected m/z ratios (b), bypass and averaged integral gas composition determined by gas chromatography (c, water amount was calculated), and averaged integral performance (d). For the axially resolved profiles, only the last five minutes for each position were considered for averaging.

### 3. Species fragmentation during mass spectrometry

The fragmentation patterns<sup>1</sup> of the observed species by gas chromatography (GC) are shown in Figure S3. For the correlation of quantified GC data with local mass spectrometry (MS) data, preferentially unique fragments for each species were used (*e.g.*,  $m/z = 22$  for  $\text{CO}_2$ ). More information about selected  $m/z$  ratios can be found in Table S1. Furthermore, the ratios of different  $m/z$  signals (*e.g.*, main fragment for allyl alcohol  $m/z = 58$ ) were checked to resolve the formation of intermediates not observed by GC. However, no clear evidence for their formation was found as the corresponding ratios were almost constant along the catalyst bed.

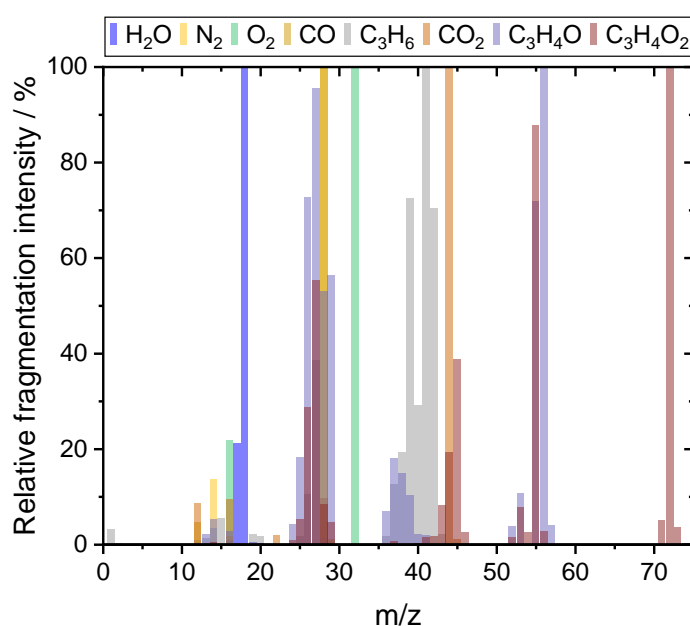


Figure S3: Species fragmentation according to the NIST database<sup>1</sup> with the intensity of each main fragment of the corresponding substance set to 100%. Columns are set transparent to visualize the complex fragmentation of the gas mixture present during selective propylene oxidation.

Table S1: Fragmentation of the reactants and observed products (by GC) in the mass spectrometer together with the selected fragment for each species for quantification of MS profile data *via* the correlation to GC data.

Substance	Fragments according to NIST database <sup>1</sup>	Selected fragment	Comment
Nitrogen (N <sub>2</sub> )	14, 28, 29	28	Assumption: only N <sub>2</sub> due to its high amount in the gas stream
Oxygen (O <sub>2</sub> )	16, 32	32	Unique fragment
Propylene (C <sub>3</sub> H <sub>6</sub> )	1, 2, 12, 13, 14, 15, 16, 19, 20, 21, 24, 25, 26, 27, 28, 36, 37, 38, 39, 40, 41, 42, 43, 44	42	Only low contribution of C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> which was neglected
Water (H <sub>2</sub> O)	16, 17, 18, 19, 20	18	Unique fragment
Acrolein (C <sub>3</sub> H <sub>4</sub> O)	13, 14, 16, 24, 25, 26, 27, 28, 29, 36, 37, 38, 39, 40, 41, 52, 53, 55, 56, 57	56	Only low contribution of C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> which was neglected
Acrylic acid (C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> )	13, 14, 15, 17, 24, 25, 26, 27, 28, 29, 30, 31, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 52, 53, 54, 55, 56, 57, 71, 72, 73, 74	72	Unique fragment
Carbon monoxide (CO)	12, 16, 28, 29	12	12 as unique fragment for CO <sub>x</sub> (CO+CO <sub>2</sub> ). Amount of CO by subtracting CO <sub>2</sub> amount from CO <sub>x</sub> .
Carbon dioxide (CO <sub>2</sub> )	12, 16, 22, 28, 29, 44, 45, 46	22	Unique fragment

## 4. Calculations

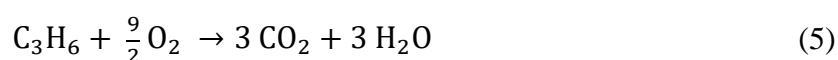
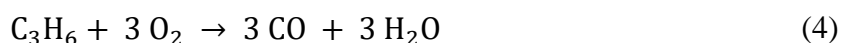
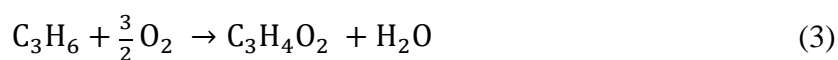
### 4.1. WHSV

The  $WHSV_{C_3H_6}$  was calculated according to equation (1).

$$WHSV_{C_3H_6} = \frac{\dot{V}_{\text{propylene}} \cdot \rho_{\text{propylene}}}{m_{\text{catalyst}}} \quad (1)$$

### 4.2. Concentration profiles

As the amount of water was not quantified by the GC, it was calculated according to the stoichiometry of the reactions leading to the observed main- and side-products (*c.f.* equations (2)-(5)).



### 4.3. Reaction progress along the catalyst bed

The propylene ( $C_3H_6$ ) conversion along the catalyst bed at position  $x$  was calculated according to equation (6). The selectivity towards acrolein ( $C_3H_4O$ ), acrylic acid ( $C_3H_4O_2$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ), and the sum of carbon oxides ( $CO_x$ ) at point  $x$  was calculated according to equations (7)-(11), respectively.

$$X_{C_3H_6}(x) = \frac{n_{C_3H_6}(-9 \text{ mm}) - n_{C_3H_6}(x)}{n_{C_3H_6}(-9 \text{ mm})} \quad (6)$$

$$S_{C_3H_4O}(x) = \frac{3 \cdot n_{C_3H_4O}(x)}{n_{CO}(x) + n_{CO_2}(x) + 3 \cdot n_{C_3H_4O}(x) + 3 \cdot n_{C_3H_4O_2}(x)} \quad (7)$$

$$S_{C_3H_4O_2}(x) = \frac{3 \cdot n_{C_3H_4O_2}(x)}{n_{CO}(x) + n_{CO_2}(x) + 3 \cdot n_{C_3H_4O}(x) + 3 \cdot n_{C_3H_4O_2}(x)} \quad (8)$$

$$S_{CO}(x) = \frac{n_{CO}(x)}{n_{CO}(x) + n_{CO_2}(x) + 3 \cdot n_{C_3H_4O}(x) + 3 \cdot n_{C_3H_4O_2}(x)} \quad (9)$$

$$S_{CO_2}(x) = \frac{n_{CO_2}(x)}{n_{CO}(x) + n_{CO_2}(x) + 3 \cdot n_{C_3H_4O}(x) + 3 \cdot n_{C_3H_4O_2}(x)} \quad (10)$$

$$S_{CO_x}(x) = S_{CO}(x) + S_{CO_2}(x) \quad (11)$$

#### 4.4. Local reaction rates

First, the total volume flow was converted to total molar flow assuming ideal gas conditions. Subsequently, the obtained value was multiplied with the individual concentration profiles (*i.e.*, points) shown in Figure S4. Thus, molar flow rates along the catalyst bed were obtained. Finally, the first derivative of these spatially resolved molar flow rates was calculated, representing the local reaction rate.



## 5. Additional profiles

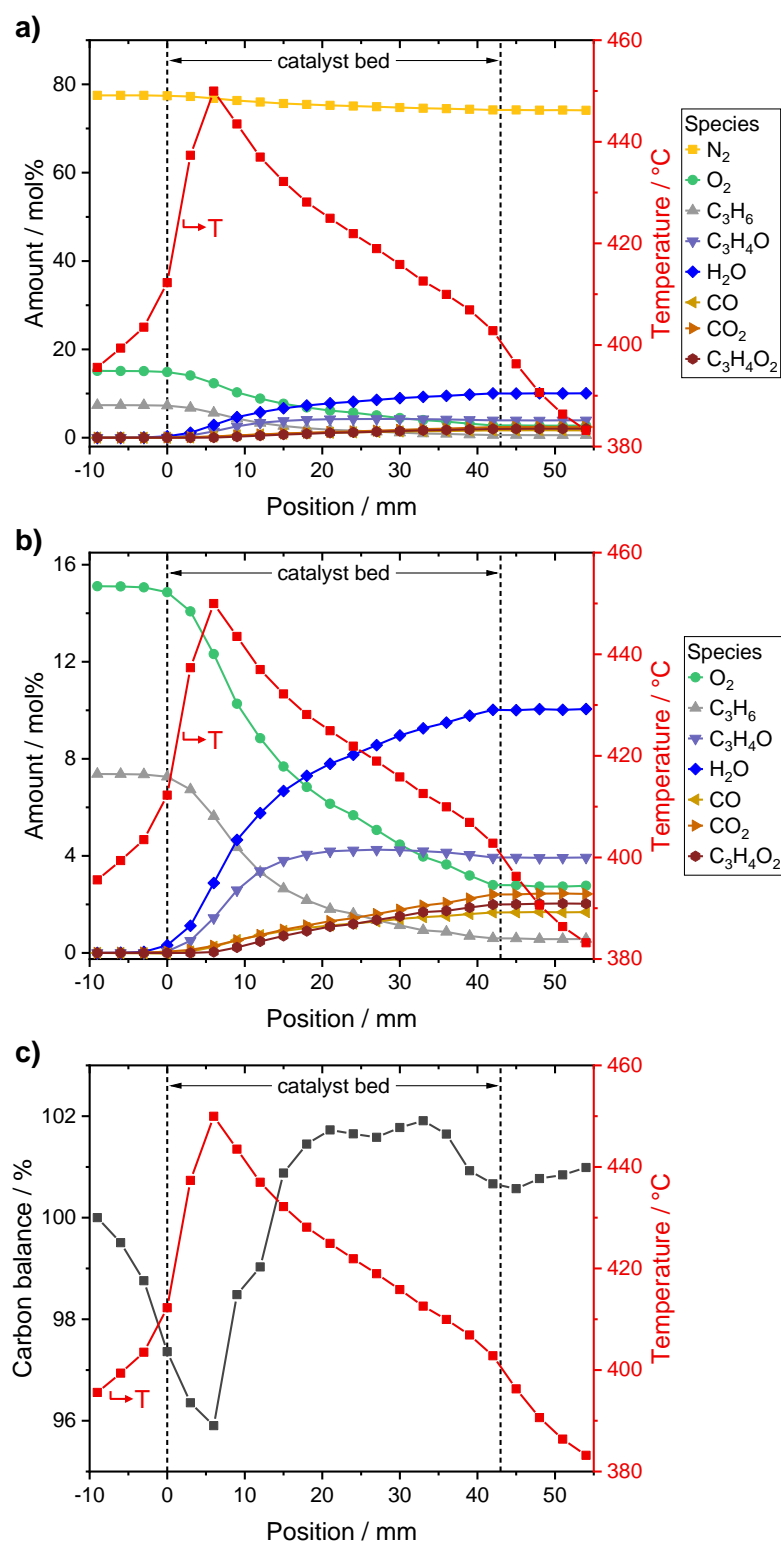


Figure S4: Concentration and temperature profiles along the packed catalyst bed during selective propylene oxidation ( $N_2/O_2/C_3H_6 = 78/14/8$  vol%,  $WHSV_{C_3H_6} = 0.29$  h<sup>-1</sup>,  $T_{oven} = 400$  °C) derived from local MS and integral GC data. Concentration profiles of all quantified species with overlaid temperature profile (a), concentration profiles for reactant and product species with overlaid temperature profile (b), carbon balance with overlaid temperature profile (c).

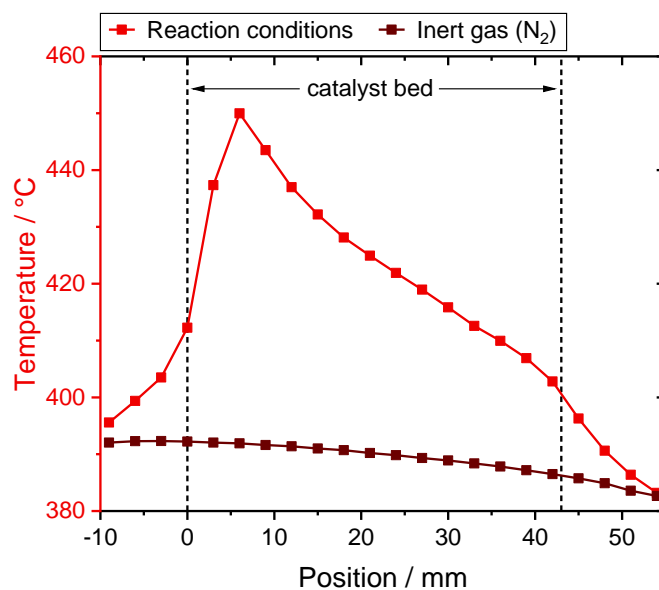


Figure S5: Comparison of temperature profile under reaction conditions ( $\text{N}_2/\text{O}_2/\text{C}_3\text{H}_6 = 78/14/8$  vol%,  $\text{WHSV}_{\text{C}_3\text{H}_6} = 0.29 \text{ h}^{-1}$ ) and under inert gas flow ( $50 \text{ mL min}^{-1} \text{ N}_2$  (same total flow)) along the same catalyst bed at an oven setpoint of  $T = 400 \text{ }^\circ\text{C}$ . The profile under inert gas flow was acquired after the profile under reaction conditions with a dwell time of 1 min per point.

## References

1. NIST Mass Spectrometry Data Center, William E. Wallace and director, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899.