



# Novel Materials for Combined Nitrogen Dioxide and Formaldehyde Pollution Control under Ambient Conditions – Supplementary Material

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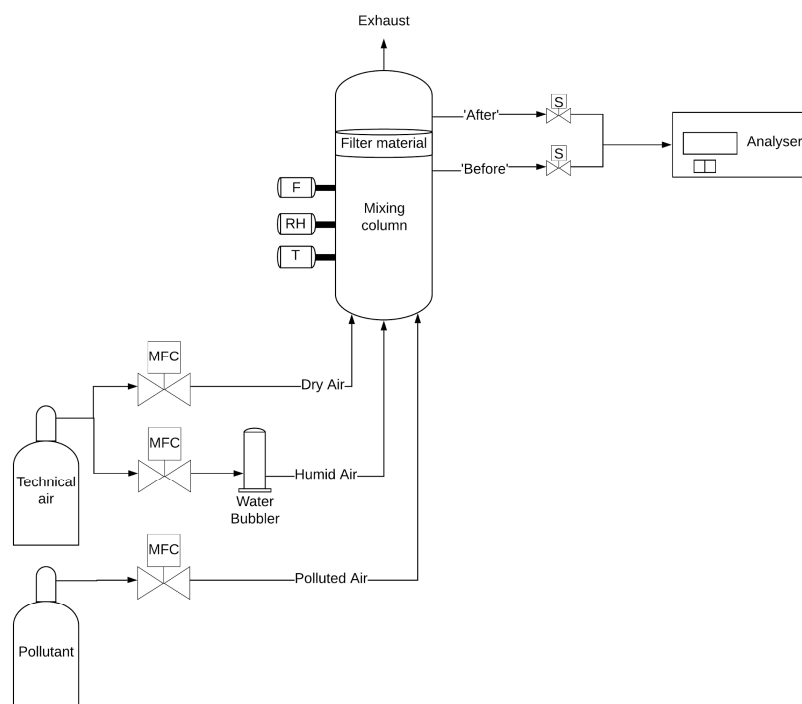


**Figure S1.** Single-pass setup schematic, for symbol key see figure S3.

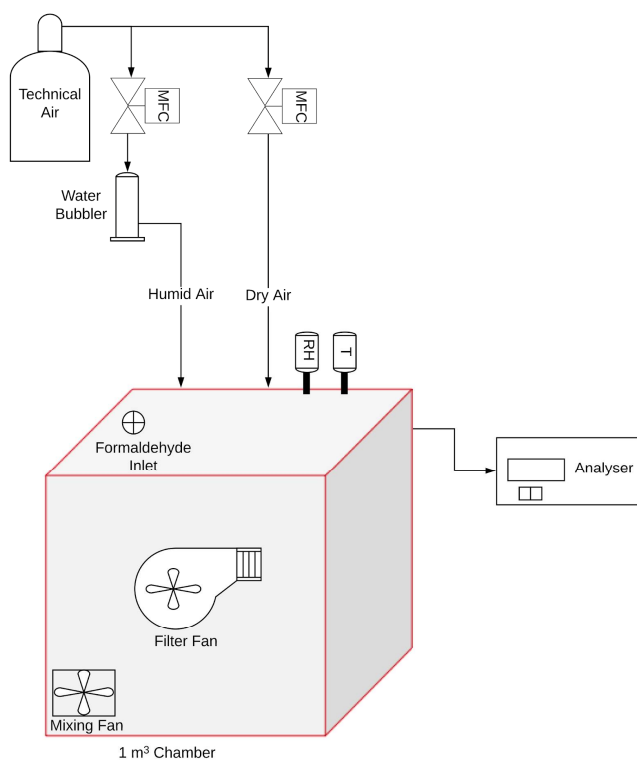


**Figure S2.** Chamber setup schematic for HCHO experiments, for NO<sub>2</sub> experiments the single pass setup was connected to an inlet on the chamber, for symbol key see figure S3.

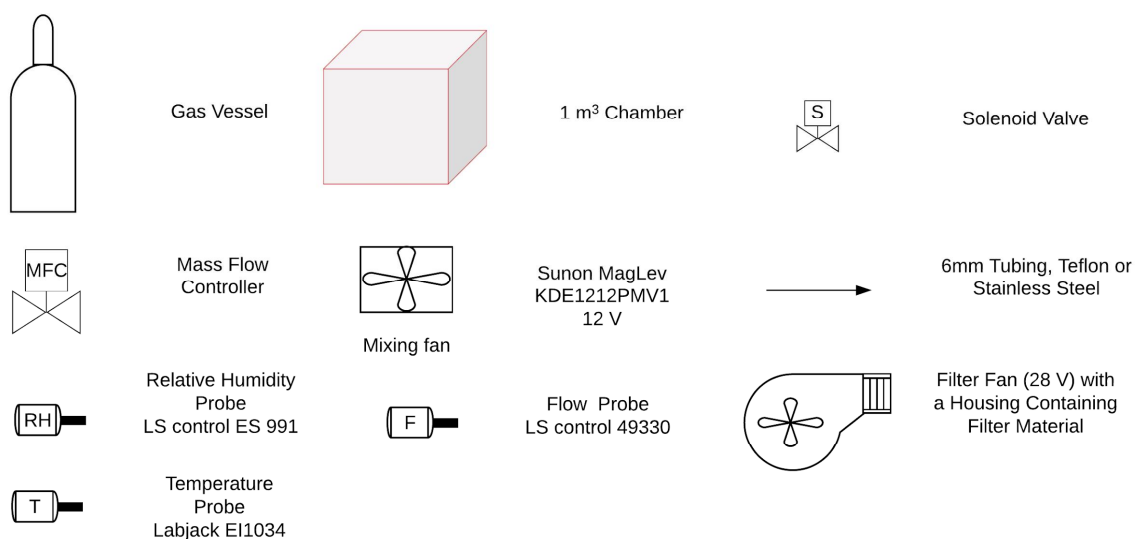


**Figure S3.** Key to symbols in figures S1 and S2.

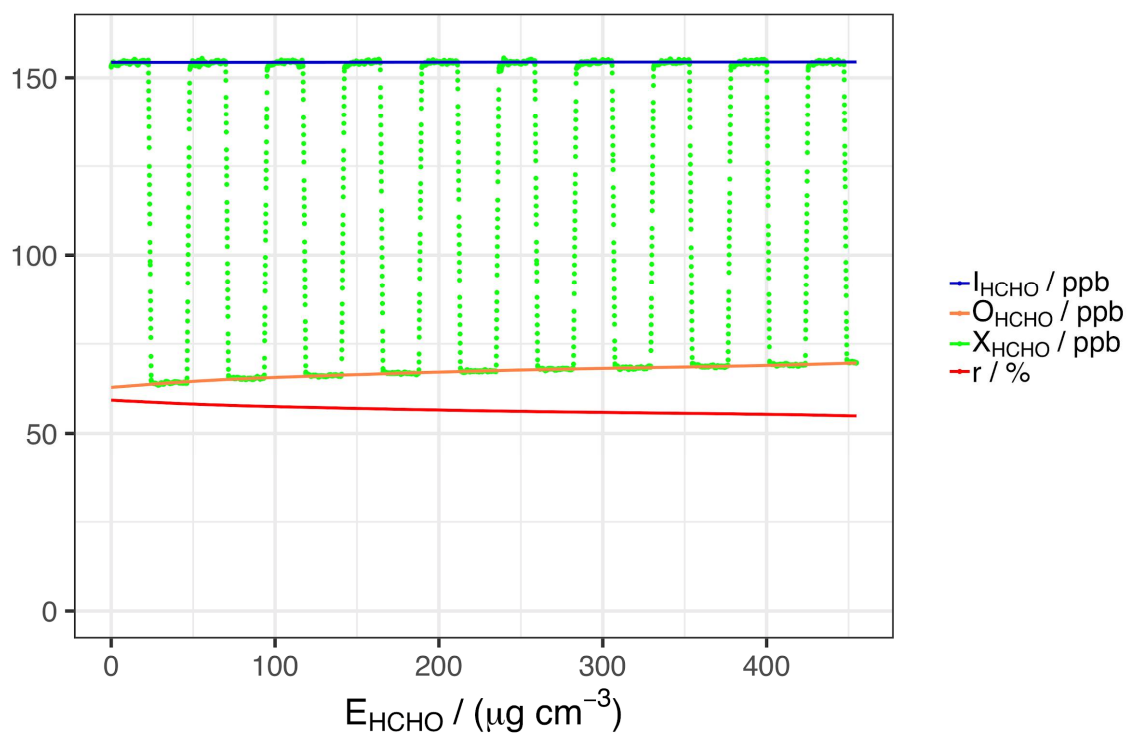


**Figure S4.** Example single-pass data recorded with the CRDS. Displaying, measured formaldehyde concentration ( $X_{\text{HCHO}}$ ), calculated inlet concentration ( $I_{\text{HCHO}}$ ), calculated outlet concentration ( $O_{\text{HCHO}}$ ) and calculated removal efficiency ( $r$ ) over a period of exposure.

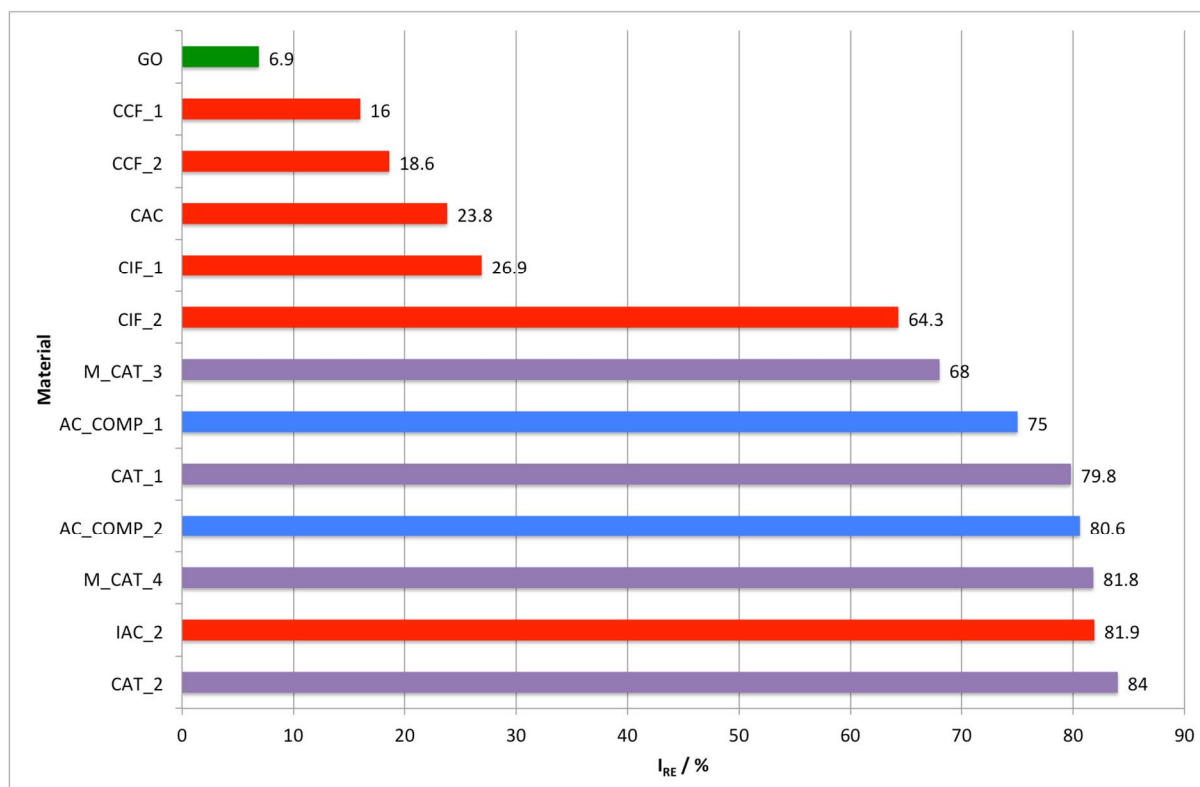


**Figure S5.** Results from the initial single-pass screening, measured with the PTR-MS. Active carbon based materials are shown in red, catalysts in purple, composites in blue and graphite oxide in green.

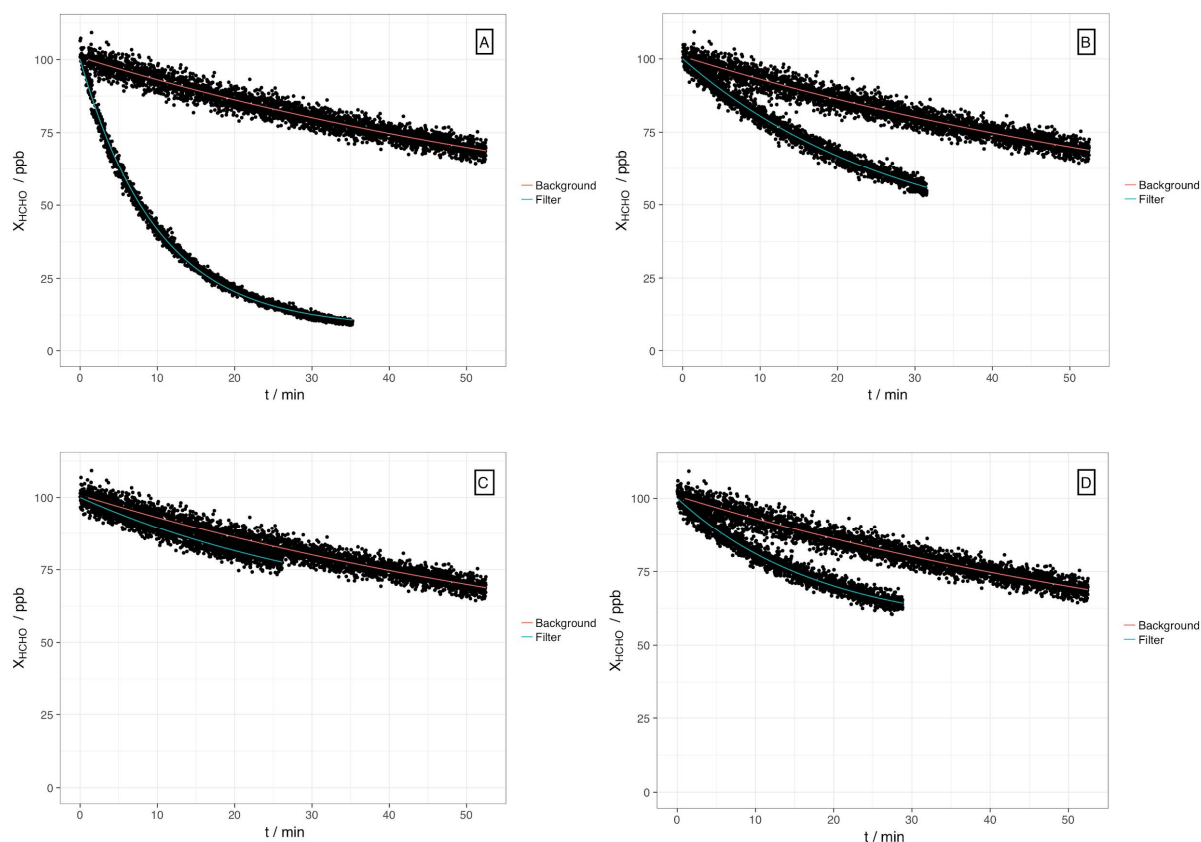


**Figure S6.** Example chamber removal data recorded with the PTR-MS. Panel A demonstrates effective removal compared to the background by the catalyst CAT\_2, panel B displays removal data for untreated CAC, panel C and D show removal data for materials IAC\_3 and IAC\_4 respectively.

**Table S1.** Averaged testing conditions (with standard deviation) and removal efficiencies (with uncertainty) for HCHO single-pass removal tests conducted with the PTR-MS.

| Material  | Volume (cm <sup>3</sup> ) | RH (%)     | Temp. (°C) | Inlet HCHO (ppb) | RE (%) at 15 µg m <sup>-3</sup> |
|-----------|---------------------------|------------|------------|------------------|---------------------------------|
| AC_COMP_1 | 3.30                      | 49.7 ± 0.1 | 19.6 ± 0.0 | 268 ± 31         | 63 ± 1                          |
| AC_COMP_2 | 2.95                      | 51.8 ± 0.6 | 19.7 ± 0.2 | 220 ± 12         | 72 ± 2                          |
| CAT_1     | 1.76                      | 49.2 ± 0.3 | 21.4 ± 0.0 | 150 ± 8          | 78 ± 1                          |
| M_CAT_4   | 2.01                      | 54.1 ± 0.2 | 20.3 ± 0.1 | 503 ± 29         | 81 ± 4                          |
| IAC_2     | 3.10                      | 54.3 ± 0.4 | 21.1 ± 0.0 | 152 ± 9          | 81 ± 2                          |
| CAT_2     | 2.36                      | 53.7 ± 0.3 | 21.2 ± 0.0 | 157 ± 15         | 82 ± 1                          |
|           |                           |            |            |                  | RE (%) at 20 µg m <sup>-3</sup> |

|       |      |            |            |          |        |
|-------|------|------------|------------|----------|--------|
| CAC   | 3.10 | 51.6 ± 0.6 | 21.2 ± 0.1 | 151 ± 7  | 5 ± 2  |
| CCF_1 | 1.23 | 48 ± 0.3   | 19.7 ± 0.0 | 410 ± 11 | 25 ± 4 |
| CCF_2 | 2.46 | 48 ± 0.2   | 19.7 ± 0.0 | 418 ± 12 | 18 ± 4 |
| CIF_1 | 4.02 | 50.3 ± 0.4 | 19.3 ± 0.1 | 390 ± 12 | 20 ± 4 |
| CIF_2 | 3.10 | 48.7 ± 0.2 | 21.4 ± 0.0 | 149 ± 8  | 39 ± 2 |

**Table S2.** Testing conditions (with standard deviation) and removal efficiencies (with uncertainty) for HCHO single-pass removal tests conducted with the CRDS in Figure 2, panel 1. The flow was set at 6.2 lpm and RH was 50 ± 5% for all tests.

| Material  | Volume (cm <sup>3</sup> ) | Temp. (°C) | Inlet HCHO (ppb) | RE (%) at 40 µg cm <sup>-3</sup> |
|-----------|---------------------------|------------|------------------|----------------------------------|
| M_CAT_4   | 2.01                      | 21.4 ± 0.2 | 130 ± 5          | 81                               |
| M_CAT_4   | 2.01                      | 21.7 ± 0.1 | 164 ± 0          | 76                               |
| CAC       | 0.62                      | 21.4 ± 0.0 | 156 ± 2          | 3                                |
| CAC       | 0.62                      | 22.2 ± 0.0 | 159 ± 5          | 3                                |
| CCF_2     | 2.46                      | 22.2 ± 0.0 | 160 ± 5          | 12                               |
| CCF_2     | 2.46                      | 20.7 ± 0.0 | 141 ± 5          | 10                               |
| AC_COMP_1 | 0.66                      | 20.6 ± 0.0 | 144 ± 4          | 35                               |
| AC_COMP_1 | 0.66                      | 21.4 ± 0.1 | 161 ± 2          | 28                               |
| IAC_2     | 0.62                      | 22.2 ± 0.0 | 151 ± 3          | 45                               |
| IAC_2     | 0.62                      | 22.1 ± 0.1 | 166 ± 3          | 43                               |

**Table S3.** Testing conditions (with standard deviation) and removal efficiencies (with uncertainty) for HCHO single-pass removal tests conducted with the CRDS in Figure 2, panel 2. The flow was set at 6.2 lpm and RH was 50 ± 5% for all tests.

| Material  | Volume (cm <sup>3</sup> ) | Temp. (°C) | Inlet HCHO (ppb) | RE (%) at 40 µg cm <sup>-3</sup> |
|-----------|---------------------------|------------|------------------|----------------------------------|
| CAT_2     | 0.47                      | 21.6 ± 0.1 | 149 ± 4          | 83                               |
| CCF_1     | 1.23                      | 20.7 ± 0.0 | 158 ± 3          | 11                               |
| CCF_1     | 1.23                      | 21.8 ± 0.2 | 155 ± 3          | 9                                |
| CIF_1     | 2.01                      | 21.9 ± 0.0 | 171 ± 2          | 14                               |
| CIF_1     | 2.01                      | 21.6 ± 0.0 | 155 ± 1          | 12                               |
| CIF_1     | 2.01                      | 21.6 ± 0.0 | 148 ± 0          | 12                               |
| AC_COMP_2 | 0.59                      | 21.9 ± 0.0 | 172 ± 1          | 42                               |

|           |      |            |         |    |
|-----------|------|------------|---------|----|
| AC_COMP_2 | 0.59 | 21.6 ± 0.2 | 143 ± 1 | 41 |
| CIF_2     | 0.62 | 21.5 ± 0.0 | 157 ± 0 | 37 |
| CIF_2     | 0.62 | 21.5 ± 0.0 | 153 ± 5 | 27 |

**Table S4.** Averaged testing conditions (with standard deviation) and removal efficiencies (with uncertainty) for NO<sub>2</sub> single-pass removal tests. Flow was set at 6.2 lpm.

| Material  | Volume (cm <sup>3</sup> ) | RH (%)     | Temp. (°C) | Inlet NO <sub>2</sub> (ppb) | RE (%) at 300 µg cm <sup>-3</sup> |
|-----------|---------------------------|------------|------------|-----------------------------|-----------------------------------|
| M_CAT_4   | 2.01                      | 46.0 ± 0.4 | 28.0 ± 0.2 | 207 ± 1                     | 8 ± 4                             |
| CAT_1     | 0.35                      | 46.0 ± 0.4 | 27.0 ± 0.2 | 207 ± 1                     | 9 ± 0                             |
| CAC       | 0.62                      | 45.8 ± 0.3 | 22.1 ± 0.0 | 201 ± 1                     | 82 ± 2                            |
| CIF_2     | 0.62                      | 45.0 ± 0.6 | 20.9 ± 0.5 | 209 ± 1                     | 98 ± 2                            |
| AC_COMP_1 | 0.66                      | 45.1 ± 1.0 | 21.4 ± 0.5 | 205 ± 1                     | 13 ± 1                            |
| AC_COMP_2 | 0.59                      | 46.1 ± 0.3 | 21.2 ± 0.1 | 204 ± 1                     | 96 ± 2                            |
| IAC_2     | 0.62                      | 45.3 ± 0.9 | 20.1 ± 0.5 | 188 ± 1                     | 79 ± 2                            |
| CAT_2     | 0.47                      | 46.0 ± 0.4 | 24.7 ± 0.2 | 207 ± 1                     | 16 ± 1                            |

**Table S5.** Testing conditions for chamber removal tests (with standard deviation) and calculated k values (with uncertainty). The test rows follow the data points in Figure 4 from right to left.

| Pollutant       | RH (%)     | Temp. (°C) | HCHO initial (ppb) | k <sub>HCHO</sub> | NO <sub>2</sub> initial (ppb) | k <sub>NO2</sub> |
|-----------------|------------|------------|--------------------|-------------------|-------------------------------|------------------|
| CO-EXP          | 49.4 ± 0.1 | 22.9 ± 0.0 | 168                | 0.094 ± 0.004     | 188                           | 0.190 ± 0.011    |
| CO-EXP          | 49.8 ± 0.0 | 22.9 ± 0.0 | 80                 | 0.099 ± 0.004     | 165                           | 0.211 ± 0.011    |
| CO-EXP          | 49.8 ± 0.1 | 22.9 ± 0.0 | 185                | 0.101 ± 0.004     | 202                           | 0.193 ± 0.011    |
| HCHO            | 47.8 ± 0.2 | 22.9 ± 0.0 | 85                 | 0.098 ± 0.004     | -                             | -                |
| HCHO            | 49.0 ± 0.1 | 23.1 ± 0.0 | 93                 | 0.091 ± 0.004     | -                             | -                |
| NO <sub>2</sub> | 49.5 ± 0.1 | 23.1 ± 0.0 | -                  | -                 | 153                           | 0.208 ± 0.011    |
| NO <sub>2</sub> | 49.3 ± 0.2 | 22.7 ± 0.0 | -                  | -                 | 191                           | 0.193 ± 0.011    |
| NO <sub>2</sub> | 50.5 ± 0.3 | 21.5 ± 0.1 | -                  | -                 | 223                           | 0.200 ± 0.011    |

**Table S6.** Mean and standard deviation of CRDS zero air tests.

| Date of test | Zero air supply            | Duration (hours) | Mean HCHO (ppb) | SD (ppb) |
|--------------|----------------------------|------------------|-----------------|----------|
| 18/01/19     | Technical air              | 1                | 0.949           | 0.870    |
| 23/01/19     | Technical air via drierite | 9                | 1.520           | 0.826    |
| 03/02/19     | Technical air              | 1                | 0.705           | 0.834    |
| 19/02/19     | Technical air              | 1                | 0.999           | 0.824    |

**Table S7.** Values calculated from nitrogen adsorption and desorption isotherms.

| Sample Name | Surface Area (m <sup>2</sup> g <sup>-1</sup> ) | Cumulative desorp. Pore Vol. (cm <sup>3</sup> g <sup>-1</sup> ) | Ave. pore radius (Å) |
|-------------|------------------------------------------------|-----------------------------------------------------------------|----------------------|
| CAT_1       | 123.3                                          | 0.386                                                           | 63.62                |
| CAT_2       | 56.1                                           | 0.416                                                           | 148.70               |
| AC_COMP_1   | 488.3                                          | 0.040                                                           | 15.70                |
| M_CAT_4     | 10.4                                           | 0.074                                                           | 40.32                |
| CAC         | 1335.0                                         | 0.573                                                           | 3.62                 |
| CIF_2       | 1289.0                                         | 0.529                                                           | 3.33                 |

Model used:

|  |       |
|--|-------|
|  | NLDFT |
|  | BJH   |
|  | BET   |

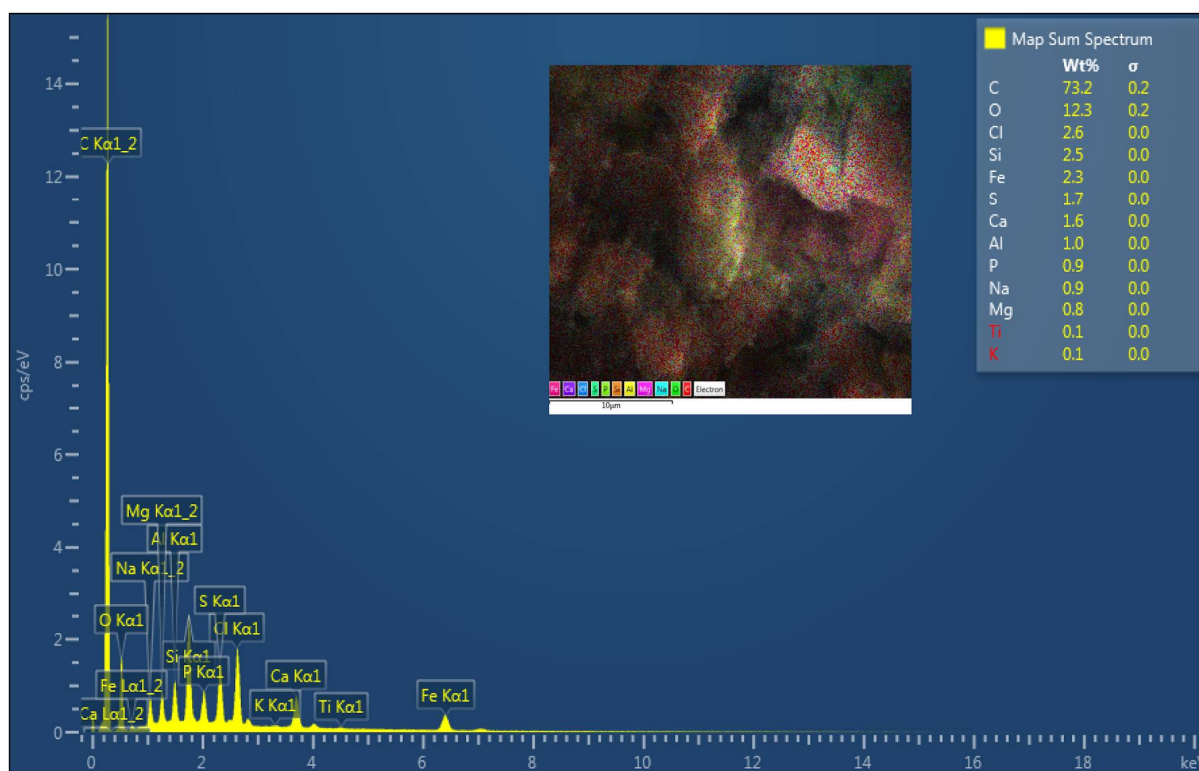


Figure S7. EDXS report for AC\_COMP\_1.

## Uncertainty determination and Instrument Comparison:

### PTR-MS

Measurement of HCHO concentration by a PTR-MS is known to vary strongly with humidity. [1,2] Therefore the instrumental uncertainty of the PTR-MS depends on the calibration of the instrument towards HCHO, and calibration of the effect of variable humidity on this instrument response.

A kinetic calibration and external calibration of the instrument were tested and the external calibration was chosen as the most appropriate method. The humidity correction factor was then determined. For the external calibration acetaldehyde was used as a surrogate for HCHO, as a permeation system for HCHO was not available. This type of surrogate calibration has been performed previously by Wisthaler et al. and was found to agree with other HCHO calibration methods within 10%. [3] A sensitivity of  $101.38667 \pm 0.036\%$  corrected counts per second (CCPS) per ppb was determined using the generated calibration curve. The stated error on the calibration gas was 5%. The uncertainty of the external calibration is determined by the propagation of the error in sensitivity and the zero, the error in the standard gasses, the error in bias (from analysis of a second standard gas against the generated calibration curve), additional error from the use of acetaldehyde instead of formaldehyde (10%) and the error in signal, the propagated uncertainty for this was 11.47%, similar to the CRDS.

However, due to the humidity dependence of HCHO measurements, a humidity correction factor (HCF) was also calculated and applied to the readings. This has an associated uncertainty which must be propagated with the error from the external calibration to give the instrumental uncertainty. In order to determine this, PTR-MS measurements of HCHO in a chamber were compared with concurrent sampling on to dinitrophenylhydrazine (DNPH) cartridges, which is a method that is not affected by increased humidity. [3,4]. This was performed in the humidity range of 30 to 65%. The derivative formed by HCHO on the DNPH cartridge was then eluted and quantified

using high performance liquid chromatography and ultraviolet spectroscopy (HPLC-UV). The comparison of these readings yielded a humidity correction factor which was determined to be:

$$\text{HCF} = 0.257 \cdot \text{AH} + 3.6722 \quad (1)$$

Where AH is absolute humidity in  $\text{g m}^{-3}$ . The error for this method depends on contributions from, the DNPH cartridges, the HPLC method, the temperature probe, the humidity probe, sampling pump time and sampling pump calibration, and was found to be 21.27%. The error in the linear regression of the humidity calibration curve must also be included (17.01%).

The uncertainty of the complete instrument calibration is then made up of the external calibration uncertainty (11.47%), the error in the DNPH-HPLC method of determining the HCF (21.27%) and the error in the linear regression of the calibration curve (17.01%), which propagate to an overall instrumental uncertainty of 29.86%. This large uncertainty applies to absolute measurements of HCHO, for instance the inlet concentration of the single-pass setup or chamber experiments. Therefore the PTR-MS results from the chamber were not used for analysis.

However in the single-pass tests an absolute measure of HCHO is not determined, rather a relative metric (removal efficiency) is used, the RH in the setup is also controlled. This means that the uncertainty in determining absolute concentrations is not a factor and the HCF can only have a minimal effect on the overall uncertainty. Therefore a less extensive uncertainty can be calculated which only takes into account the non-linear parts of the external calibration (leaving just the signal) and the minimal RH changes, but includes UC from the experimental setup.

The average UC from the signal was found to be 0.33%. For consideration of RH related UC the test with the largest deviation in RH was found (AC\_COMP\_2, 0.63% RH change). The HCF was then calculated for the minimum and maximum inlet and outlet concentrations for this test and applied. The difference between the highest and lowest possible RE due to this RH change was then calculated to be 0.82% or  $\pm 0.41\%$  about the calculated RE. In order to take into account other aspects of the experimental setup repeat tests of the same sample were compared and the average standard deviation for the calculated RE at each point was found. It was seen that the packing of different sample morphologies was the greatest factor in determining the uncertainty. A total uncertainty was then calculated by propagating these errors. In this way a different relative experimental uncertainty for each sample form was determined from repeat single-pass experiments for HCHO and  $\text{NO}_2$  removal experiments and combined with the instrument uncertainty to yield a total uncertainty. UC related to different material forms are shown in table S8.

**Table S8.** Experimental uncertainty contribution from different sample morphologies.

| <i>Material Morphology</i> | <i>RE Uncertainty (%)</i> |
|----------------------------|---------------------------|
| <i>AC bead</i>             | 1.6                       |
| <i>AC pellet</i>           | 0.9                       |
| <i>Composite</i>           | 1.6                       |
| <i>Mounted powder</i>      | 4.3                       |
| <i>Rounded grain</i>       | 0.4                       |
| <i>Cylindrical grain</i>   | 1.0                       |

### Chemiluminescence $\text{NO}_x$ Analyser

As mentioned above the uncertainty for  $\text{NO}_2$  measurement was calculated by first calibrating the instrument and determining an instrumental uncertainty and then combining this with an

experimental uncertainty based on repeat experiments to give a total uncertainty for the measurement.

For the instrument calibration a calibration setup was built so that the flow from a certified 50.9 ppm NO<sub>2</sub> bottle could be mixed with technical air in the correct proportions, through the use of mass flow controllers, for a zero and scale calibration of the NO<sub>x</sub> analysers to be performed. A heated molybdenum catalyst that could achieve total conversion of NO<sub>2</sub> to NO was also added, allowing NO<sub>2</sub>, NO and total NO<sub>x</sub> readings to be calibrated individually.

## CRDS

The CRDS from Picarro is factory calibrated and has a precision of 1.2 ppb + 0.1% of the reading for HCHO readings, with no dependence on humidity levels. It has a lower limit of detection of 0.3 ppb (upper is 30 ppm) and zero drift may be up to 1.5 ppb per 24 hours, however no significant drift in zero level was seen during this testing period (shown in table S6). Meaning that the UC for the instrument in relative tests (e.g. single-pass RE determination) is as above. For the determination of absolute concentrations of HCHO, for instance during chamber testing, the accuracy is  $\pm 10\%$ .

An additional experimental uncertainty was not calculated, due to the limited number of experiments, instead all of the experimental data was plotted, with the difference in repeat tests of individual materials (up to 16% difference in RE) shown. The main source of this UC is deemed to be due to differences in packing between the samples tested, which were of a low total volume in order to better separate the results for effective materials with high RE. This increased the UC relative to earlier tests is due to packing differences however.

## Chamber Experiments

For the chamber tests the uncertainty in the  $k$  values is expressed as the root of the mean variance over all experiments for that species.

## Bibliography:

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- [4] T. Salthammer, S. Mentese, Comparison of analytical techniques for the determination of aldehydes in test chambers, *Chemosphere*. 73 (2008) 1351–1356.



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