SpaciMS - probing what is hidden within

Spatial and temporal *operando* resolution of catalytic monoliths

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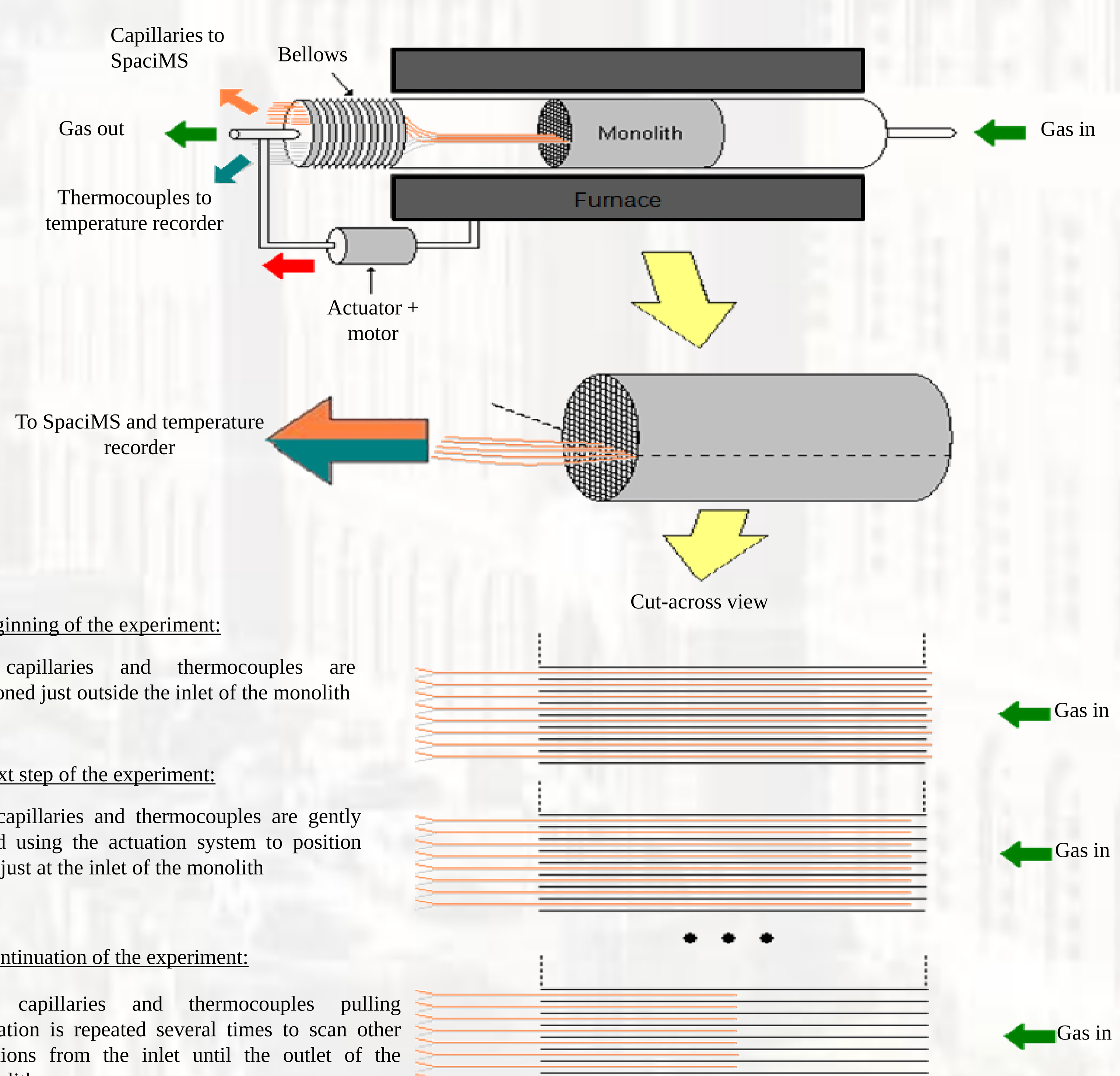
1. Introduction

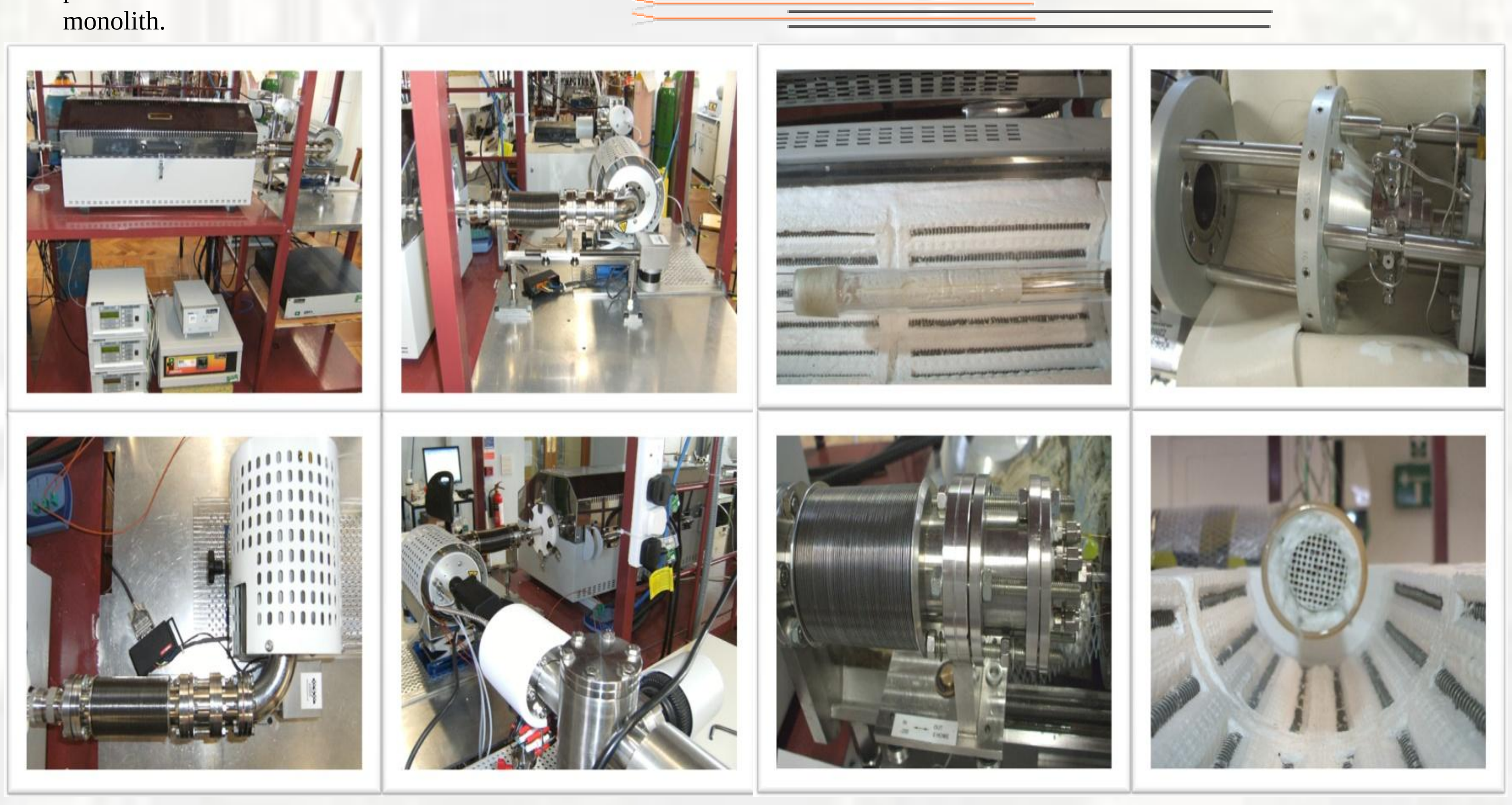
Under working conditions, structured catalysts exhibit spatial and temporal distributions of the chemical species and temperature, that often lead them to operate under sub-optimal conditions. Although the investigation of catalysts under real reaction conditions has been of interest for many years there have been only few genuine examples of *operando* studies techniques. The development of a minimally invasive system,[1,2] probing inside of a monolith, aims at revealing what is happening inside the 'black box'. The **SpaciMS** consists in a spatially resolved capillary-inlet mass spectrometry, which uses thin fused-silica capillaries and thermocouples inserted axially into the monolith channels. The **SpaciMS** is used to obtain axial and radial information about chemical species (i.e. reactants, products and intermediates) and temperatures, giving access to mechanistic information and 3D maps of working catalysts. In this work we report on the latest development of the **SpaciMS** technique and address the concerns about technique sensitivity and probes invasiveness.

2. Objectives

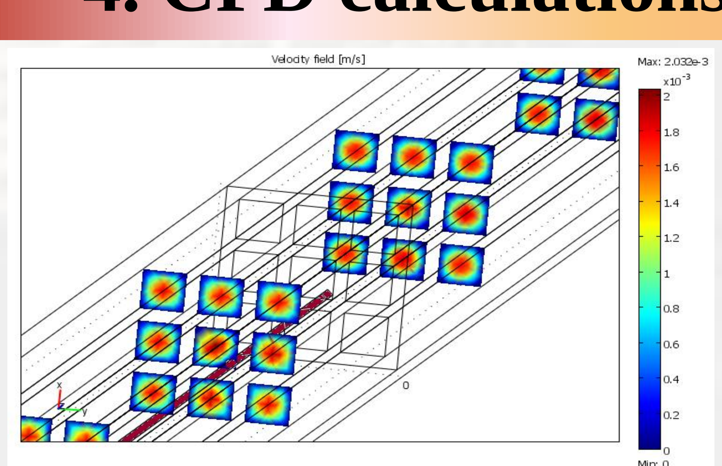
- ❑ Development of an innovative analytical technique for investigation of real, structured materials (e.g. monoliths) under realistic reaction conditions
- ❑ Addressing different problems related to structured catalysts by spatially resolved capillary inlet spectrometry (SpaciMS)

3. SpaciMS instrument and experiment

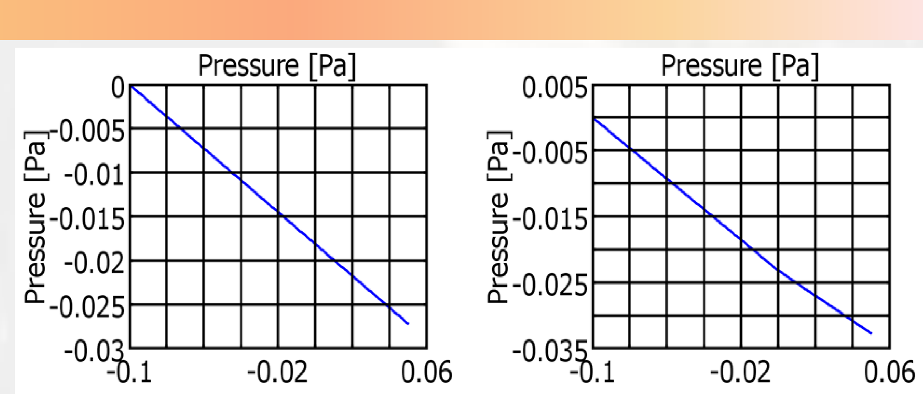




4. CFD calculations

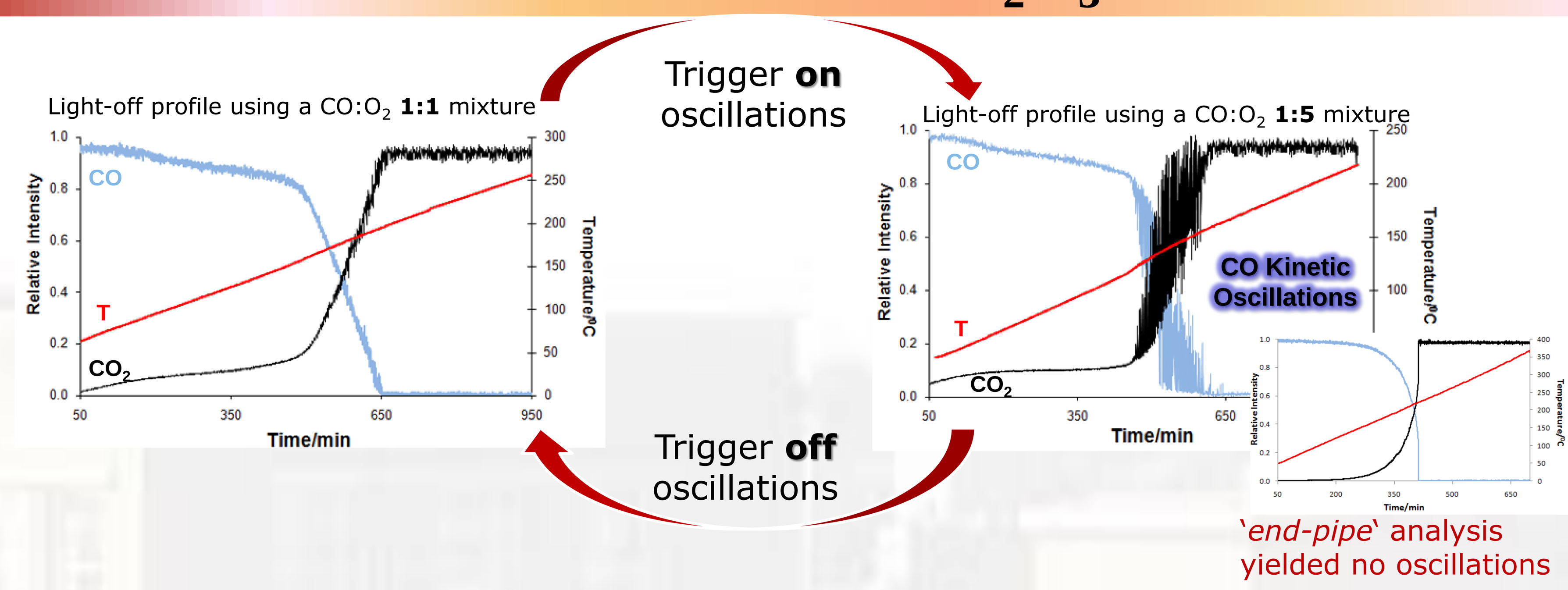


Gas distribution and velocity inside the monolith channels.



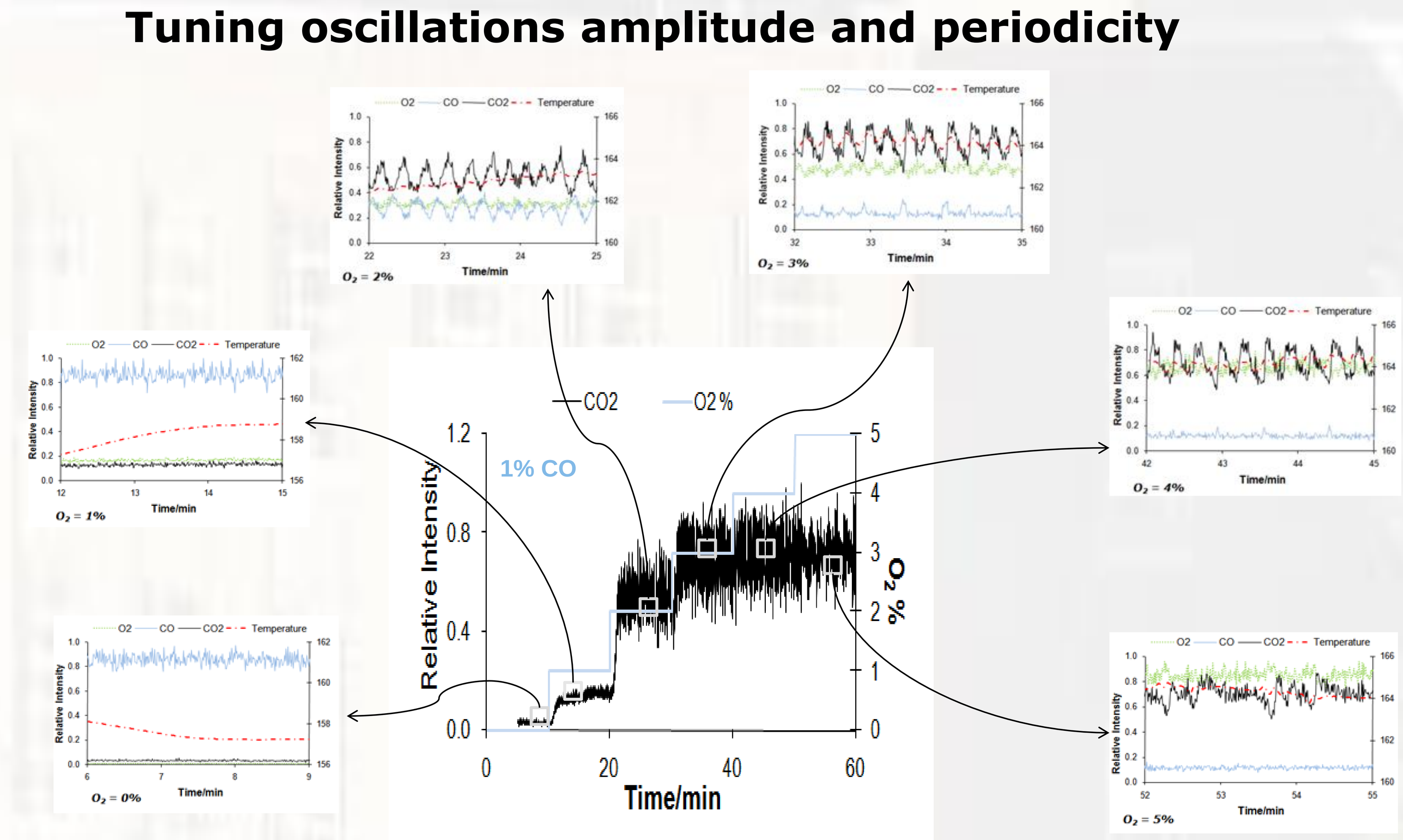
Probes influence in the overall pressure drop of the gas inside the channel. Without probe (left) and with a 250 μm probe (right).

5. CO oxidation over Pt-Rh/Al_2O_3 monolith

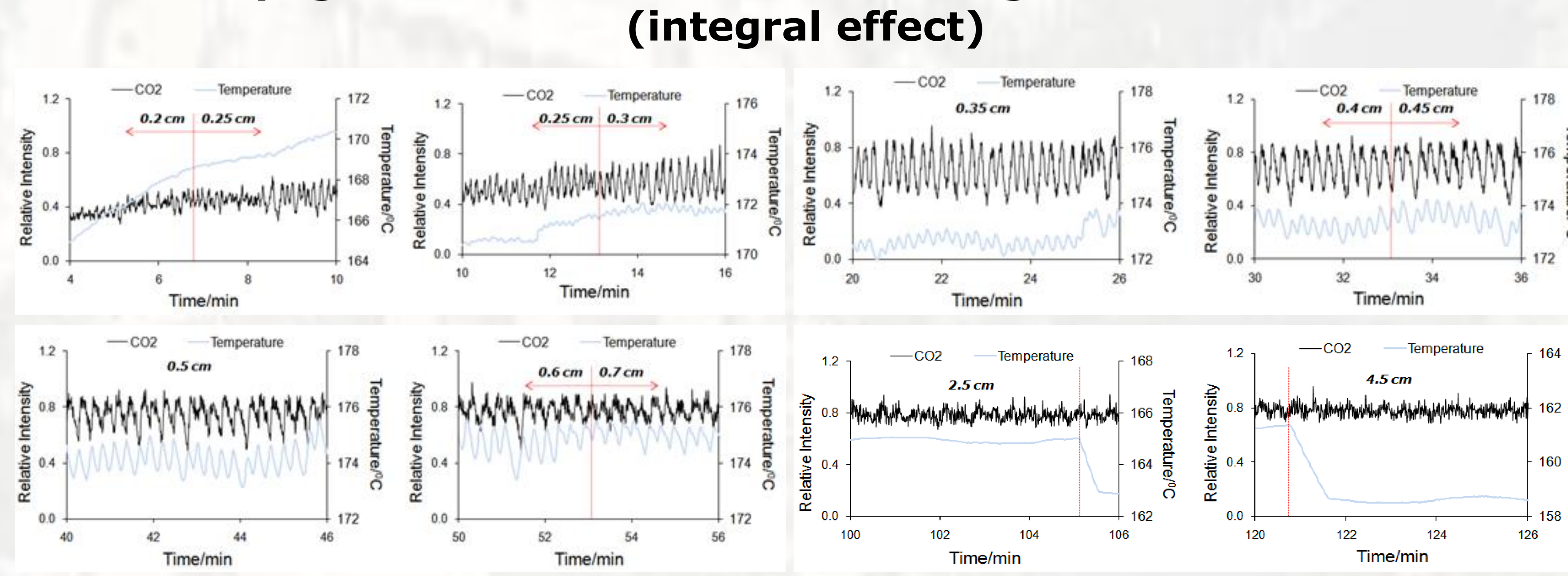


'*end-pipe*' analysis yielded no oscillations

Tuning oscillations amplitude and periodicity



Propagation of the oscillations throughout the monolith (integral effect)



6. Summary.

✓ Kinetic oscillations during CO oxidation were measured, suggesting high sensitivity and spatial resolution of the technique.
✓ Amplitude of the oscillations can be tuned by changing the CO:O_2 ratio in the feed.
✓ Amplitude and frequency are not independent, generally they vary inversely and are dependent on the CO:O_2 ratio and the conversion[3].
✓ Periodicity of oscillations in the CO_2 signal was de-phased by half a period relative to the CO.

7. References

[1]W. P. Partridge, J. M. E. Storey, S. A. Lewis, R. W. Smithwick, G. L. DeVault, M. J. Cunningham, N. V. Currier, T. M. Yonushonis, ***SAE Technical Paper*** 2000-01-2952, 2000.
[2] J. –S. Choi, W. P. Partridge, C. S. Daw, ***Appl. Catal. A*** 293 (2005) 24.
[3] G. Ertl, ***Science***, 254 (1990) 1750.
[4] P-A. Calrsson, V. P. Zhdanov, M. Skoglundh, ***Phys. Chem. Chem. Phys.*** 8 (2006) 2703.

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