An *in-situ* spatially resolved method to probe gas phase reactions through a fixed bed catalyst.

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1- Description of the set-up

Figure S1 and S2 is a representation of the technique that can be divided in five main elements:

- Tubular reactor (Catalyst bed)
- Sampling unit (Capillary)
- Linear motion drive system
- Vacuum chamber and MS
- Heating system

![3D representation of the Spatial Resolution Set-up](image1)

**Figure S1:** 3D representation of the Spatial Resolution Set-up

![Picture of the Spatial Resolution Set-up](image2)

**Figure S2:** Picture of the Spatial Resolution Set-up
The packed catalyst bed (11 mm in length) is loaded in a quartz tubular reactor (20 cm length, 3 mm I.D., 5 mm O.D.) compressed between two beds of silicon carbide secured by quartz wool to keep the catalyst bed packed (see Figure 2).

The sampling unit or drilled capillary consists of a very thin synthetic fused silica capillary (150 μm O.D., 75 μm I.D., Polymicro Technologies) that has been drilled (by Laser Micromachining Limited) in the side-wall using laser ablation (shown in Figure 3b). The diameter of the holes is approximately 20 μm. The capillary is directly connected to the vacuum chamber via a home designed adaptor, which has been welded on a flange. This adaptor holds the capillary and avoids any leak in the vacuum system from that connection.

The manual linear transfer mechanism provided by VG Scienta consists of a bellow which can be extended or compressed manually via a rotary valve; it allows movement with 0.5 mm precision with a total range of movement of 5 cm.

The vacuum system is composed of two chambers and each one is connected to a turbo molecular pump (Pfeifer Vacuum, TMU 521 DN), each backed by a mechanical pump (Pfeifer Vacuum, DUO 10 M), which creates the ultra-high vacuum (1.2 x 10^{-8} torr). Two vacuum chambers are necessary in order to get an appropriate pressure for the normal use of the quadrupole mass spectrometer (Hiden HPR20).

The heating of the reactor is achieved via a hot air blow heater (leister, Le Mini). This innovative heating system provides the additional advantage of visual access to the reactor, which will allow the coupling of the spatial resolution technique with a number of spectroscopic techniques in the future. The temperature was monitored using a type K thermocouple placed on the surface of the reactor.

2- Catalyst preparation

1wt% Pd/Al₂O₃ was prepared using wet impregnation from bis-(benzonitrile) palladium (II) chloride using γ-Al₂O₃ (Grace Davison). The catalyst testing was conducted using 100 mg of catalyst with a particle size between 250-450 μm giving a catalyst bed ength of 11 mm. Prior to each experiment the catalyst was oxidized at 500 °C for 30 min under flow of dry air.

3- Insertion of the capillary

The flexibility and fragility of the capillary does not allow direct insertion into the catalyst bed. To overcome this problem, a “loading” capillary (350 μm O.D., 200 μm I.D.) is used to create a channel in the catalyst bed which the drilled capillary can go through easily. The next step is to slowly remove the loading capillary from the catalyst bed, leaving only the sampling capillary. The differences of diameter between the two capillaries creates some space between the sampling capillary...
and the catalyst bed, where gases might channel, thus affecting the results. In order to avoid channelling a re-packing of the catalyst bed is required.

4- Calculation of conductance in viscous regime

The conductance through an aperture in the viscous regime equation is:

\[ C_v = (136 \times d^4) \times \left( \frac{P}{L} \right) \]  

(Equation S1)

where \( C_v \) is conductance in \( \text{L s}^{-1} \)
\( d \) is the diameter of the aperture in cm
\( P \) is the pressure difference from inlet to outlet (overestimated at 1000 mbar)
\( L \) is the length of the capillary (25 cm)

For the i.d. of the capillary (0.0075 cm)
\[ C_v = (136 \times (0.0075^4)) \times (1000/25) = 1.72 \times 10^{-5} \text{ L s}^{-1} \text{ or } 1.03 \text{ mL min}^{-1} \]

5- Gas concentration

CO oxidation was conducted using a total gas flow rate of 100 cm\(^3\) min\(^{-1}\) (1% CO and 0.525% O\(_2\) balance Ar). For reactions in the presence of H\(_2\) a total gas flow rate of 100 cm\(^3\) min\(^{-1}\) (0.3% H\(_2\), 1% CO and 0.68% O\(_2\) balance Ar) was used.

6- Experiment

In a typical experiment, the holes of the drilled capillary are positioned upstream of the catalyst bed. Then the reactor is moved mm by mm deeper into the catalyst bed using the Z-motion drive, the dwell between two points is 5 min in order to be sure that the signal is stable. This operation is repeated until the full scan of the catalyst bed while the MS is analysing the gas. Similarly, in a separate test a thermocouple has been placed in the catalyst bed so that the temperature profile could be reported during the reaction in the absence and presence of H\(_2\).
7- Results

**Figure S2**: CO conversion in the catalyst bed at different temperatures; 150 °C (▬), 200 °C (▪), 225 °C (□), 250 °C (●) and 300 °C (▲). The catalyst bed is represented by the shaded area.

**Figure S3**: CO conversion in the catalyst bed at different temperatures in presence of hydrogen; 150 °C (▬), 200 °C (▪), 225 °C (□), 250 °C (●) and 300 °C (▲). The catalyst bed is represented by the shaded area.

**Figure S4**: CO$_2$ yield in the catalyst bed at different temperatures in presence of hydrogen 150 °C (▬), 200 °C (▪), 225 °C (□), 250 °C (●) and 300 °C (▲). The catalyst bed is represented by the shaded area.
Figure S5: Evolution of the temperature in the catalyst bed at 250 °C; with H₂ (▬) and without (▬). The catalyst bed is represented by the shaded area.