An *in situ* Spatially Resolved Method to Probe Gas Phase Reactions and Temperature Through a Fixed Bed Catalyst

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Introduction

Catalysts have different shapes and forms depending on their use.

Understanding the phenomena that occur within a catalytic reactor during the reaction is necessary to improve catalyst efficiency.
Most commonly, catalytic studies use “end pipe” sampling, i.e. gas are sampled after catalyst bed for analysis.

Consequence, the catalyst is seen as a black box where limited information on gas and temperature can be extracted.
Introduction

Techniques recently developed with spatially resolved on *operando* condition

- Spaci-MS for catalytic monolith developed by QUB and Oak Ridge *et al.*
- Spatial resolution of catalytic foam developed by the University of Minnesota

But, so far no technique has been developed for spatially resolved gas and temperature from packed catalyst bed
Gas sampling and temperature recording

Drilled capillary inserted in the catalyst bed
Sampling occurs through the lateral holes
Thermocouple inserted in the capillary
Capillary is connected to the MS vacuum chamber
Other end is sealed
Principle of the spatial resolution

Reactor is moved mm by mm by an automated stage
Capillary is sampling gas
Thermocouple is recording temperature of the gas sampled
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Consequently, the gas concentration and temperature profile in the catalyst bed are obtained operando
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Characteristic of the capillary:
- 250µm O.D.; 100µm I.D.
3 pairs of sampling holes (diameter 20µm), 180° spacing
- Within 0.5 mm

Capillary drilled by laser ablation using Xenon focused ion beam (Plasma-FIB)

Invasiveness of the capillary?
Cross section area of the capillary is 0.7 % of the cross section area of the reactor (I.D. reactor: 3 mm, O.D. capillary: 250 µm)
Thermocouple

Characteristic of the Thermocouple:
- 80 µm O.D. (Okazaki, Japan)

Thermocouple is inserted in the capillary
Tip is aligned with the holes
Position of the thermocouple is maintained during the experiment
Spatial resolution system
Spatial Resolution System

- Vent
- Bellow 1
- Reactor
- Bellow 2
- Gas Inlet
- Ceramic Plate
- Automated Stage
- Heater Adapter
- Heater
How invasive is the technique?

The pressure drop without capillary is 114.7 Pa and 125.5 Pa with capillary which represent 0.057% and 0.062% respectively of the total pressure.
Reaction: \( \text{CO} + 0.5 \text{O}_2 = \text{CO}_2 \)  
Conditions: CO= 1\%, O\(_2\) = 20\%; Total flow: 100mL/min at 200 ℃  
Catalyst: 1\%Pt/Al\(_2\)O\(_3\), 50 mg, Length : 8 mm Particles size: 250-425 μm
Evolution of the CO$_2$ yield

Reaction: CO + 0.5 O$_2$ = CO$_2$
Conditions: CO= 1%, O$_2$= 20%; Total flow: 100mL/min at 200, 175, 150 and 125 °C
Catalyst: 1%Pt/Al$_2$O$_3$, 50 mg, Length : 8 mm Particles size: 250-425 μm
Reaction: $\text{CO} + 0.5 \text{O}_2 = \text{CO}_2$

Conditions: $\text{CO} = 1\%$, $\text{O}_2 = 20\%$; Total flow: 100mL/min at 200, 175, 150 and 125 °C

Catalyst: 1%Pt/Al$_2$O$_3$, 50 mg, Length : 8 mm Particles size: 250-425 μm
Micro-kinetic model

The micro-kinetic model for CO oxidation is based on the kinetic expressions reported by Hauptmann et al. The results obtained for the gas concentration show a good fit between experimental and simulated. The temperature results need to be refined as the model was originally developed for monolith.

Conclusion

The spatially resolved technique developed allowed to obtained gas and temperature profile *operando* within a packed catalyst bed with minimal invasiveness.

The CFD calculations have determined the probe to be minimally invasive.

Good fit was obtained between the experimental profiles and a micro-kinetic model concerning gas concentration but the model needs to be refined for the temperature as the heat and mass transfer parameters used are those for a monolith rather than powder.

Further development of the spatially resolved technique with combination of spectroscopic technique is possible due to the innovative heating system.
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