Probing pellet-scale reaction-diffusion phenomena in a trickle bed reactor using *operando* magnetic resonance spectroscopic imaging

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Highlights

- *Operando* magnetic resonance imaging of intra-pellet composition at 86 μm resolution
- Partial wetting causes significant asymmetry in conversion at the pellet-scale
- 1D reaction-diffusion models fail to describe composition at pellet-scale
- *Operando* measurements provide novel insight into pellet-scale reaction-diffusion

1. Introduction

In heterogeneous catalysis, the distribution of reactant and product species within a catalyst pellet are of central importance to the catalyst performance, and ultimately to the overall conversion and selectivity realized in commercial-scale reactors. Despite this importance, fundamental understanding of pellet scale behaviour at operando conditions is limited due to the coupled, multi-scale nature of the underlying transport processes, and the limited techniques capable of mapping the intra-pellet composition at industrially relevant length scales. Here, we demonstrate the coupling between transport and reaction at the pellet scale by using *operando* magnetic resonance spectroscopic imaging (MRSI) to map the liquid composition within $Pd/\gamma\text{-}Al_2O_3$ catalyst pellets at an isotropic in-plane spatial resolution of 86 μm during a styrene hydrogenation reaction. The objective of this work is to develop and apply a magnetic resonance method to achieve the *operando* measurement of intra-pellet composition at the pellet scale. Slice-selective MRSI is implemented with compressed sensing to enable the acquisition of quantitative two-dimensional (2D) maps of the concentration profile within operating catalyst pellets. The resulting images reveal that partial wetting of the catalyst pellet significantly influences the intra-pellet composition profile. The measurements reported in this work give the first direct experimental insight into the effect of partial wetting on the concentration profile within an operating catalyst pellet.

2. Methods

The reaction studied in this work was the hydrogenation of styrene to ethylbenzene over a 0.5 wt% Pd/Al_2O_3 catalyst. Cylindrical catalyst pellets (3.2 mm diameter) were loaded into a 5 mm diameter fluoropolymer tube which was subsequently placed inside the bore of a 7.0 T superconducting magnet (Figure 1a). Gaseous hydrogen and liquid styrene flow were introduced to the bed at a flow rate of 1.0 NL h^{-1} and 0.02 mL min^{-1}, respectively. Slice-selective MRSI [1] was conducted to acquire 2D spatially resolved maps of the intra-pellet chemical composition. To image the bed structure and the inter-pellet liquid distribution, 3D rapid acquisition with relaxation enhancement (RARE) imaging [2] was used. Imaging was conducted at an isotropic resolution of 86 μm with a field-of-view (FOV) of 5.5 mm (x) × 5.5 mm (y) × 22 mm (z) for 3D acquisitions, and a FOV of 5.5 mm (x) × 5.5 mm (y) with a slice thickness of 2 mm for 2D acquisitions.

3. Results and discussion

The bed structure and inter-pellet fluid in the reactor during operation at steady state are shown in Figure 1b. Note that successive repeat 3D images of the inter-pellet liquid revealed the liquid structure to be stable, with very minimal change observed for images taken 10 h apart (not shown). The inter-pellet liquid in the bed is seen to partially wet the surface of the catalyst pellet, which is well known for both single pellet string reactors and commercial-scale trickle bed reactors [3]. The clear wetting inhomogeneity presents an excellent opportunity in this study for evaluating how wetting inhomogeneity at the pellet-scale impacts composition and reaction heterogeneity at the pellet-scale.

A map of the intra-pellet ethylbenzene (product) concentration for the bottom-most pellet in the reactor is shown in Figure 1c. The composition map in Figure 1c was computed directly from nuclear magnetic resonance (NMR) spectra measured in each voxel (not shown). The composition map in Figure 1c gives clear evidence of the coupling between transport and reaction on the pellet-scale. In this gas-limited reaction, the reaction readily proceeds on the side of the pellet directly exposed to hydrogen. However, on the gas exposed side the ethylbenzene produced can only be removed by evaporation, which due to the low vapor pressure is very limited. As a result, to leave the pellet the ethylbenzene accumulates on the gas-exposed side and diffuses towards the liquid-wet side, causing a concentration gradient across the entire pellet. This interpretation corresponds well with the simulations conducted by Tang *et al.* [4] for a gas-limited reaction. The results reported here reveal the significant reaction heterogeneity caused by partial wetting of a catalyst pellet. Clearly, the composition within the pellet is highly non-symmetric, demonstrating that commonly used 1D reaction-diffusion models are inadequate to describe reaction-diffusion in trickle beds at the pellet-scale.

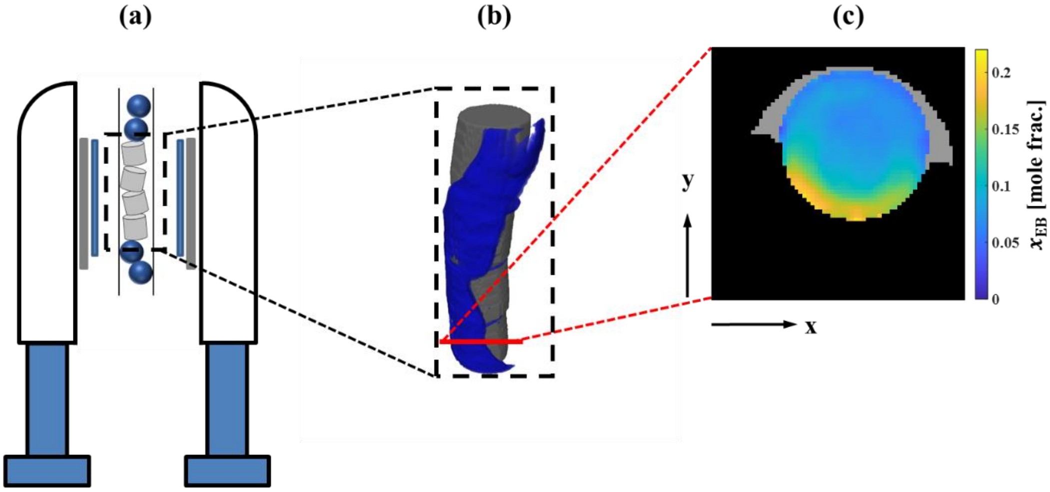

Figure 1. Use of *operando* magnetic resonance techniques to study wetting and composition at the pellet-scale. (a) schematic representation of *operando* magnetic resonance setup. (b) 3D image of bed structure and liquid wetting. Blue shading represents inter-pellet liquid while grey shading represents catalyst pellets. (c) 2D map of intra-pellet ethylbenzene concentration. Image resolution and field-of-view is given in in Section 2.

4. Conclusions

Pellet-scale intra-pellet composition maps acquired at an in-plane resolution of 86 μm during *operando* styrene hydrogenation reveal the direct coupling between wetting, mass transport, and reaction. The results reported here provide unique experimental insight into the complexity of reaction-diffusion phenomena at the pellet-scale within an operating reactor. The magnetic resonance methods implemented here, and the resulting insight provided, have the potential to aid in the further optimization of the wetting and transport properties of commercial catalysts. Specifically, these magnetic resonance methods provide a new experimental capability for direct measurement of pellet-scale transport and reaction behaviour for heterogeneously catalysed reactions, and for aiding the development of reaction-diffusion modelling techniques which accurately capture the effects of partial wetting.

References

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Keywords
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