

***Operando* Magnetic Resonance Studies of Fischer-Tropsch Catalysis in a Trickle-Bed Reactor**

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Highlights

- First *operando* imaging of Fischer-Tropsch reaction occurring in a fixed-bed reactor.
- Spatially mapping of product evolution.
- Reaction followed as a function of time-on-stream of 4 days.
- Spatial mapping of molecular diffusivity of products.

1. Introduction

Fischer-Tropsch (FT) synthesis is a heterogeneous catalytic process that converts synthesis gas ($\text{CO} + \text{H}_2$) to linear hydrocarbons and is commercially applied as the central part of the gas-to-liquid (GTL) process [1]. Improving the performance of the reaction process remains a long-standing challenge in both industry and academia because this requires understanding of the way the system behaves at the scales of both the reactor and catalyst. The motivation for this work is to understand what is happening inside the pore space of catalyst pellets operating in a narrow fixed-bed reactor. To achieve this, a number of different magnetic resonance (MR) experiments have been implemented to spatially map product evolution and the characteristic molecular diffusion coefficients of molecular species within the bed. The advantage of magnetic resonance in this application is that it is non-invasive and can acquire two-dimensional (2D) and three-dimensional (3D) images of optically opaque media. Further, it is able to characterise chemical composition and transport properties such as molecular diffusion. Application to Fischer-Tropsch synthesis is particularly challenging because of the large number of chemically-similar products that will exist within the reactor. The present study reports the first *operando* application of MR measurements to a FT reaction occurring over a supported ruthenium catalyst, operating in a pilot scale trickle-bed reactor.

2. Methods

The reaction was carried out in continuous flow in a fixed-bed reactor of inner diameter 20 mm, placed inside the magnet of a SWB 300 MHz Bruker spectrometer. The reactor was operated at 220 °C and 36 barg. Extrudate pellets of a 1 wt% Ru/TiO₂ catalyst of 1-3 mm in length were packed in the reactor in 3 layers, each of 3 mm thickness. To dilute the bed, a packing of silicon carbide of height 10 mm was used to separate each catalyst layer. The catalyst was first reduced *in situ* under an H₂ atmosphere at 250 °C and 2 barg for 30 h. Subsequently, the reactor was cooled to the reaction temperature and pressurised to 36 barg under a H₂/N₂ flow. Syngas was introduced in down-flow with a feed composition (mol ratio) of H₂:CO:N₂ = 6:3:1 and a space velocity of 3.6 NI/(h g_{cat}), where g_{cat} is the grams of catalyst in the reactor. The FT reaction was operated for a total time-on-stream (TOS) of 4 days, resulting in an overall conversion of approximately 35%. The reactor off-gas (CO, CO₂, N₂, H₂, light hydrocarbons (C₁-C₅)) was analysed by means of an online GC (Agilent, 7890B RGA). *Operando* MR measurements were carried out to map product distribution through the reactor and the molecular diffusivity of these molecules during reactor operation.

3. Results and discussion

Figure 1 (a) shows the MR image acquired from a vertical slice through the reactor at TOS = 4 days. ¹H MR signal intensity is indicated by the intensity scale bar. Lighter shades indicate a larger concentration of ¹H-containing species. These images do not identify specific molecular species. The signal intensity is dominated by signal associated with liquid phase species; this is because MR measures the number of

nuclear spins (i.e., ^1H species), and typical liquid phase densities are ~ 3 orders of magnitude higher than gas phase densities. It is clearly seen that liquid phase products exist within the catalyst pellets and that products build up in the inter-particle space towards the bottom of the reactor. Transverse image sections through the reactor are shown in Figure 1(b). These images are of the same slice section through the reactor at TOS = 2 and 4 days, respectively. These images show that at TOS = 2 days the products that exist in the lowest layer of catalyst packing has remained inside the catalyst pellets. However, after 4 days, signal intensity and therefore products are seen all around the wall of the reactor. Spatially-resolved and unresolved measurements of molecular diffusivity within the bed reveal two-components throughout the bed. The slower of these is shown in Figure 1(a) from the data recorded TOS = 4 days. This slower component of molecular diffusivity is seen to increase down the reactor and is consistent with an increase in chain length of the product species down the bed. These data combined with spatially-resolved spectroscopy, giving insight to product distribution, and nuclear spin relaxation time measurements which characterise the interaction of molecular species with the pore surface give additional insights into the way the system evolves with time.

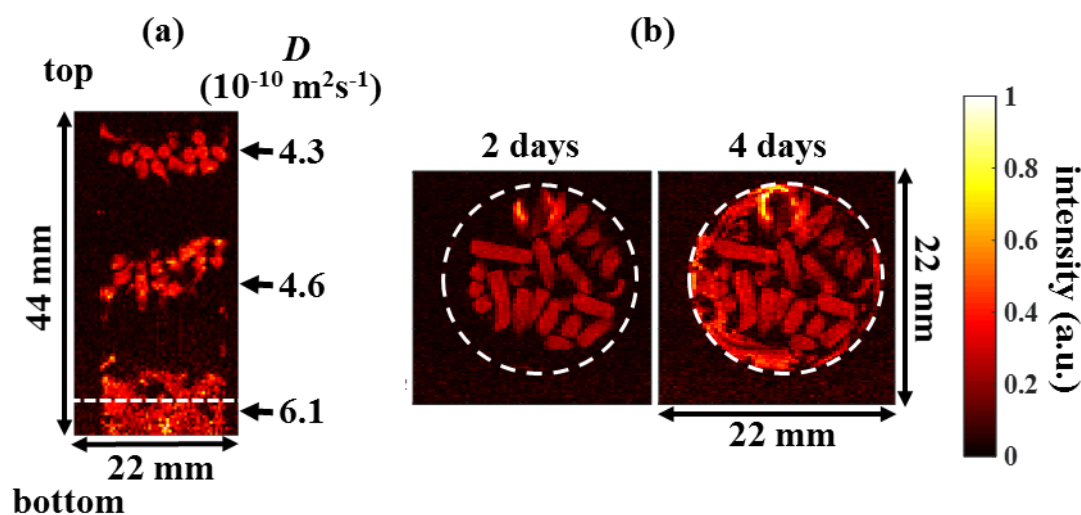


Figure 1. (a) MR image of a vertical slice within the reactor, acquired at TOS = 4 days. The three layers of the catalyst bed are clearly identified. The flow direction is from top to bottom. (b) Images of a transverse slice through the bottom layer of catalyst packing acquired at 2 and 4 days of reaction, respectively. The position in the bed at which the transverse images are acquired is indicated by the dashed white line in (a). The image signal intensities are on the same intensity scale; thereby confirming the build-up of products in the bed as a function of TOS, and the existence of waxy products around the inner wall of the reactor. The reactor wall is identified by the dashed white line.

4. Conclusions

This work reports the first *operando* MR study of FT catalysis occurring in a narrow fixed-bed reactor. The reactor was operated at 220 °C and 36 barg for a time-on-stream of 4 days. MR imaging identified product formation throughout the bed and the accumulation of products in the lower section of the reactor. A combination of ^1H MR imaging with spatially-resolved measurements of nuclear spin relaxation and molecular diffusion give new insights into processes occurring at both the pore-scale of the catalyst and at the reactor scale.

References

- [1] D.A. Wood, C. Nwaoha, B.F. Towler, J. Nat. Gas Sci. Eng. 9 (2012) 196-208.

Keywords

Fischer-Tropsch Synthesis; *Operando* measurement; NMR; MRI.