

Hysteresis in the selectivity to long-chain products during Fischer-Tropsch synthesis occurring in wax-saturated catalyst pellets

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Highlights

- Hysteresis in the selectivity to long-chain products observed when varying feed H₂/CO ratios.
- Correlation identified between C₅₊ selectivity and product composition inside catalyst pellets.
- The extent of hysteresis increases along the reactor axial direction.

1. Introduction

Fischer-Tropsch synthesis (FTS) enables the production of synthetic hydrocarbons and chemicals from syngas (CO and H₂) which is produced using non-fossil resources. The performance of FTS is significantly affected by operating conditions. However, how the reaction behaviour is influenced by the operating history, specifically the hysteresis behaviour, is not well understood. In this study, we identify a hysteresis in the selectivity to long-chain hydrocarbons during FTS occurring in catalyst pellets and when the feed H₂/CO ratio is cycled between 2 and 0.5. The hysteresis is observed for both the product composition confined inside the catalyst pellets as determined by *operando* magnetic resonance imaging (MRI) and for the C₅₊ selectivity as measured by online gas chromatography (GC).

2. Methods

The FTS reaction was carried out in a fixed bed reactor of inner diameter of 20 mm and packed with three layers of 1 wt% Ru/TiO₂ catalyst pellets which are cylindrical extrudate pellets of diameter 2 mm and length 5 mm. The catalyst bed was diluted with non porous inert silicon carbide (SiC) particles to achieve isothermal operation. The packing structure is indicated in Fig. 1a. The reaction was operated at 220 °C, total pressure of 37 bar and a weight hourly space velocity (WHSV) of 4000 NL h⁻¹ g_{cat}⁻¹. The feed H₂/CO ratio was varied in the sequence 2→1→0.5→1→2. The effluent gas composition was determined using an online GC (Agilent Refinery Gas Analyser 7890B-0378).

The *operando* MRI measurement was achieved by placing the reactor, which is constructed of a non-magnetic ceramic material (silicon nitride), in the magnet of a Bruker Avance III HD spectrometer which has a vertical super-wide bore 7.1 T magnet and a gradient set providing a maximum gradient strength of 83.24 G cm⁻¹ in three orthogonal directions. A birdcage radio frequency (r.f.) coil of 66 mm inner diameter was used and tuned to a resonance frequency of 300.14 MHz for ¹H. The diffusion coefficients of hydrocarbon products at local catalyst layers were spatially resolved by combining pulsed field gradient (PFG) and MRI techniques [1]. The diffusion measurement results were then converted to the carbon numbers of the products [2].

3. Results and discussion

The C₅₊ selectivities at the steady state for different H₂/CO feed ratios are shown in Fig. 1b. It is observed that C₅₊ selectivity increases with decreasing feed ratio. The selectivities obtained when the feed ratio is increased from 0.5 to 2 are higher than those previously measured at the same condition during the decrease of feed ratios, suggesting a hysteresis in C₅₊ selectivity. The variation of C₅₊ selectivity after the feed ratio is increased to 2 from 1 is presented in Fig. 1c. The selectivity first decreases rapidly after the feed ratio is increased until reaching a minimum of 90.3% which is comparable with the selectivity of 90.1% measured during the first run at feed ratio 2 (indicated by the horizontal dashed line). The C₅₊ selectivity then increases gradually over time and stabilises at 91.6% after ~300 h of operation. This

non-monotonic variation leads to the hysteresis in C_{5+} selectivity (Fig. 1b). It has been reported that the catalyst pellets at the steady state are saturated by liquid products [1]. The variation of the average carbon number, \bar{N}_C , of the intra-pellet liquid products is determined by *operando* MRI and shown in Fig. 1c. The \bar{N}_C decreases simultaneously as the C_{5+} selectivity increases, suggesting correlation between the two properties. This correlation strongly indicates that the increase in C_{5+} selectivity can be attributed to a reduction in the extent of diffusion limitation for H_2 and CO inside the liquid-saturated pellets as the \bar{N}_C decreases, which leads to a decrease in the H_2/CO ratio in pores and hence an increase in C_{5+} selectivity. The distributions of \bar{N}_C of intra-pellet products at the three catalyst layers are measured by *operando* MRI and the results obtained at feed ratio of 1 are shown in Fig. 1d. At all catalyst layers, the \bar{N}_C measured during the increase of feed ratios is higher than that determined during the decrease of feed ratio. The extent of this hysteresis increases along the reactor axial direction. Despite the hysteresis identified for the selectivity to long-chain products, no obvious hysteresis is observed for the CO conversion.

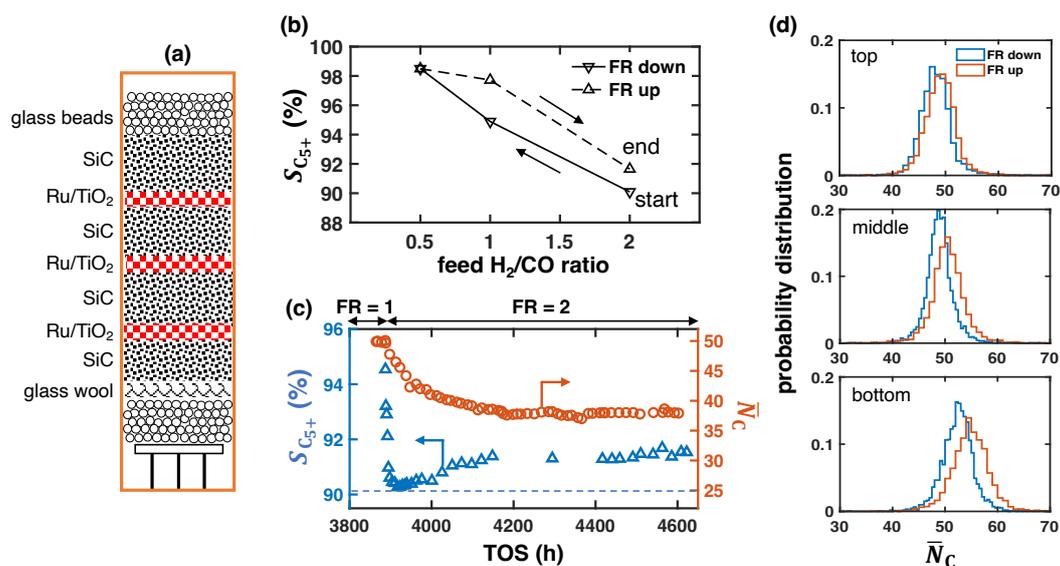


Figure 1. (a) Packing structure of the reactor. (b) C_{5+} selectivity, $S_{C_{5+}}$, determined at the steady states of different feed ratios (FR). The arrows indicate the direction of the variation of FR. (c) Variation of C_{5+} selectivity and the average carbon number, \bar{N}_C , of intra-pellet liquid products measured after the feed ratio is increased to 2 from 1. The time periods of operating at feed ratio 1 and 2 are indicated at the top of the figure. (d) Distributions of the \bar{N}_C of intra-pellet liquid at the three catalyst layers. The results determined at the second (FR up) and first run (FR down) at feed ratio 1 are compared.

4. Conclusions

Hysteresis in the selectivity to long-chain products is identified for FTS occurring in catalyst pellets saturated by liquid wax products. *Operando* MRI and online GC measurements reveal a correlation between the C_{5+} selectivity and the average carbon number of intra-pellet liquid products, providing strong evidence that the hysteresis behaviour is attributed to the diffusion limitation of H_2 and CO inside the catalyst pellets. The extent of hysteresis increases along the axial direction of the reactor. This work suggests that the selectivity of FTS can be tuned by novel reaction operation.

References

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Keywords

Hysteresis; Fischer-Tropsch synthesis; *operando*; magnetic resonance