

## Water Condensation in a Wax-Saturated Porous Silica Operating at Conditions Relevant to Fischer-Tropsch Synthesis

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### Highlights

- Evidence of water condensation in wax-saturated pores under FT-relevant conditions.
- *Operando* measurement of the amount of water condensation in wax-saturated pores.
- *Operando* measurements of water and wax diffusivities in pores.
- Estimation of volume and surface area of pore space occupied by water.

### 1. Introduction

Water is the primary by-product of Fischer-Tropsch (FT) synthesis which has been commercially applied to produce linear hydrocarbons from syngas, and it is well known that water has a significant and complicated influence on the performance of FT catalysts [1]. Under typical low temperature FT conditions catalyst pores are considered to be saturated with FT wax. This work explores the phase behaviour in such pores as increasing amounts of water vapour are introduced in to the fixed bed. In particular, nuclear magnetic resonance (NMR) is used to characterise the phase behaviour in the pore space of a typical silica catalyst support and estimate the extent to which water displaces wax and interacts with the silica surface. During a catalytic process such behaviour would be expected to impact catalyst performance significantly. The present work reports an experimental NMR study of the water-wax phase behaviour in a porous silica saturated by a model wax, n-octacosane (n-C<sub>28</sub>). NMR techniques enable *operando* measurements of the relative amount of water and wax in the silica pores and the diffusion properties of the two chemical species.

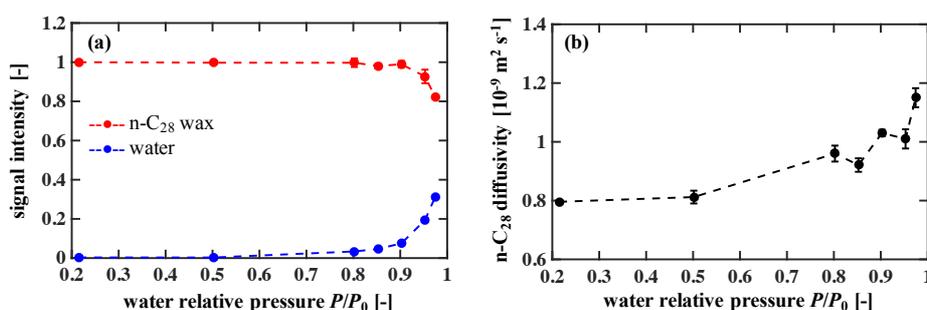
### 2. Methods

To prepare the wax-saturated silica, silica pellets with an average pore diameter of 18 nm were first dried and then soaked in excess amount of n-C<sub>28</sub> liquid at 90 °C for 12 h to ensure full saturation. The wax-saturated pellets were then packed in a cylindrical column which was placed in the bore of a Bruker AV 300 NMR spectrometer. The temperature in the packed column was controlled at 195 °C and the wax-saturated silica pellets in the bed were exposed to a flow of gas-phase water, the pressure of which was increased in the range of 3–13.6 bar corresponding to a water relative pressure  $P/P_0$  of 0.2–0.97. The gas pressure in contact with the silica was allowed to stabilise prior to NMR data acquisition. The temperature was selected to be close to that for low temperature FT synthesis, while allowing good temperature and pressure control. Further, the n-C<sub>28</sub> vapour pressure at this temperature was low enough to avoid evaporation.

A range of NMR techniques were used as follows. The NMR signal intensity associated with the wax and water species was acquired using the spin-echo pulse sequence [2]. Diffusivities of n-C<sub>28</sub> and water were measured using a 13-interval alternative pulsed-gradient stimulated echo (APGSTE) pulse sequence [3] and the NMR  $T_1$  relaxation time was measured using a saturation recovery sequence [4].

### 3. Results and discussion

Figure 1 (a) presents the NMR signal intensities, which are proportional to the amount of molecules, of n-C<sub>28</sub> wax and water in the silica pores. It is observed that the water intensity slowly increases with increasing pressure at  $P/P_0 < 0.9$  and shows a sharp increase with pressure at  $P/P_0 > 0.9$ , which suggests capillary condensation of water. The intensity of the wax signal decreases rapidly at  $P/P_0 > 0.9$  when condensation of water occurs, suggesting replacement of intra-pellet wax by water. Figure 1 (b) shows the diffusivities  $D$  of n-C<sub>28</sub> in pores measured at various water pressures. The  $D$  values of n-C<sub>28</sub> increase with increasing water pressure from  $8 \times 10^{-10}$  to  $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  indicating increased mobility of n-C<sub>28</sub> molecules as water invades the pore space. The pore volume and surface fractions occupied by water in the wax-saturated pores can also be estimated by combining the NMR intensity measurement and the N<sub>2</sub> adsorption analysis of the silica. The fractions of water-occupied volume and surface are calculated to be as high as 33% and 42%, respectively.



**Figure 1.** (a): Signal intensities of n-C<sub>28</sub> wax and water in the silica pores as a function of the relative pressure of water. The intensities in (a) were normalised to the intensity of n-C<sub>28</sub> at  $P/P_0 = 0.21$ . (b): Diffusivities of n-C<sub>28</sub> in the porous silica as a function of the relative pressure of water.

### 4. Conclusions

This work provides experimental evidence of water condensation in wax-saturated pores under FT relevant conditions, and achieves *operando* measurement of the amount and diffusivities of intra-pellet water and n-C<sub>28</sub> wax in the pore space of a typical porous silica catalyst support. The pore volume and surface occupied by water were also estimated from the NMR measurement results.

### References

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### Keywords

Fischer-Tropsch synthesis; effect of water; phase behaviour; NMR