

## ***Operando* Measurement of Intra-Pellet Compositions in Multiphase Systems using Magnetic Resonance**

Qingyuan Zheng\*, Andrew J. Sederman, Lynn F. Gladden

University of Cambridge, Department of Chemical Engineering and Biotechnology, West Cambridge Site,  
Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom

\*Corresponding author: qz240@cam.ac.uk

### **Highlights**

- *Operando* measurement of intra-pellet liquid and gas compositions.
- Results reveal insights into adsorption and vapour liquid equilibrium in pores.
- Spatial mapping of intra-pellet compositions down a fixed-bed reactor.
- Changes in reaction selectivity can be tracked along the reactor.

### **1. Introduction**

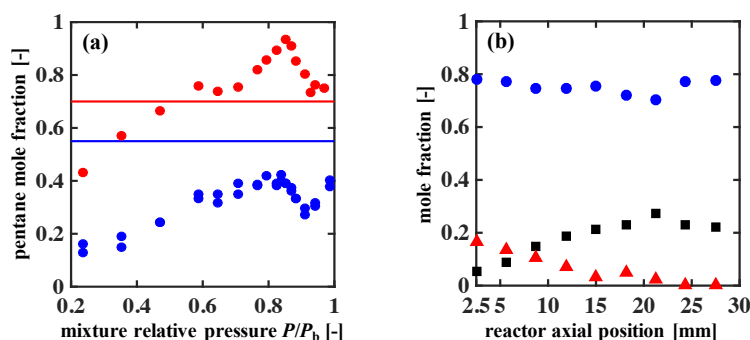
In heterogeneous catalysis, catalyst performance is directly influenced and reflected by the composition and phase of the molecular species in the pore space of the catalyst. Conventional techniques, such as gas chromatography, can only measure the mixture composition in the inter-pellet space which is different from that of intra-pellet mixtures because of mass transfer limitation. This presentation reports the development and application of nuclear magnetic resonance (NMR) techniques that enable *operando* measurement of intra-pellet compositions. It is shown that the NMR signal acquired from the two environments may be distinguished either by the diffusion coefficient or the NMR spectral lineshape of the inter- and intra-pellet species. The characteristic which allows discrimination of chemical species is system-dependent. Two case studies are reported. First, differences in molecular diffusion coefficient are used to discriminate and measure compositions of intra-pellet liquid and gas mixtures, and hence to study the vapour liquid equilibrium of a methanol-pentane mixture in a porous silica. Second, differences in NMR lineshape between species in the intra- and inter-pellet space during 1-octene hydrogenation occurring in a fixed-bed of Pd/Al<sub>2</sub>O<sub>3</sub> catalyst enable the measurement of intra-pellet chemical compositions while reaction is occurring.

### **2. Methods**

In the study of the methanol-pentane system, silica pellets of pore size 20 nm were exposed to a flow of methanol-pentane feed gas of 2 different compositions:  $x_{\text{pentane}} = 55 \text{ mol\%}$  and  $70 \text{ mol\%}$ . For each feed composition, the system temperature was controlled at  $130 \text{ }^\circ\text{C}$  and pressure was allowed to stabilise at 19 pressure steps in the range of 2-17 bar. At each pressure step, NMR measurements were performed to acquire the NMR <sup>1</sup>H signal intensities and the diffusivities of the two molecular species. A novel data analysis method was developed to obtain the compositions of intra-pellet liquid and gas mixtures. In the 1-octene hydrogenation study, the measurements were performed under ambient conditions on a fixed bed of 0.3 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst pellets under conditions of co-current downflow of 1-octene liquid and a 50/50 mol% H<sub>2</sub>/N<sub>2</sub> gas mixture characterised by liquid and gas Reynolds numbers:  $0.2 < Re_L < 0.6$  and  $0.1 < Re_G < 0.3$ . The reaction was operated under H<sub>2</sub>-lean conditions with the feed mole ratios of 1-octene/H<sub>2</sub> = 11/1 and 21/1. To obtain intra-pellet compositions along the length of the reactor, a partial least square regression method was developed and implemented such that discrimination of inter- and intra-pellet species could be achieved based on the analysis of their respective lineshape characteristics [1].

### 3. Results and discussion

Figure 1 (a) presents the intra-pellet liquid compositions of methanol-pentane mixtures as a function of the relative pressure of the gas mixture in the system. The intra-pellet gas compositions were measured to be the same as the feed compositions and are not shown in the figure. For the results obtained for the two feed gas compositions of  $x_{\text{pentane}} = 55 \text{ mol\%}$  and  $70 \text{ mol\%}$ , the pentane fractions at low pressure are smaller than the feed compositions indicated by the two horizontal lines, suggesting that the intra-pellet fluid is in adsorption equilibrium (ADE) with the pore surface with preferential adsorption of methanol. At high pressure, the liquid compositions show the opposite trend with a methanol- and pentane-rich liquid formed in the pore space for the  $55 \text{ mol\%}$  and  $70 \text{ mol\%}$  feeds, respectively. This suggests capillary condensation of gas mixtures and vapour liquid equilibrium (VLE) in pores. The contrasting results for the two feed compositions at high pressure implies an azeotrope composition between  $x_{\text{pentane}} = 55 \text{ mol\%}$  and  $70 \text{ mol\%}$ . Further, the increase in pentane fractions with increasing pressure in the low pressure region for both feed compositions indicates a transition from ADE to VLE. Figure 1 (b) presents the intra-pellet compositions of the ternary reaction mixture of 1-octene, 2-octene and n-octane, along the length of the reactor during liquid-phase 1-octene hydrogenation. It is observed that the major reaction product switches at  $\sim 10 \text{ mm}$  down the reactor from the hydrogenation product (n-octane) to the isomerisation product (2-octene).



**Figure 1.** (a): Compositions of intra-pellet liquid of methanol-pentane mixtures for feed gas compositions of  $x_{\text{pentane}} = 55 \text{ mol\%}$  (●) and  $x_{\text{pentane}} = 70 \text{ mol\%}$  (●). The feed compositions of  $55 \text{ mol\%}$  and  $70 \text{ mol\%}$  are indicated by the blue and red horizontal lines, respectively.  $P_b$  is the bubble point pressure of mixtures. (b): Intra-pellet compositions of the reaction mixture along the length of the reactor obtained during 1-octene hydrogenation, where ● = 1-octene, ■ = 2-octene, ▲ = n-octane.

### 4. Conclusions

NMR techniques have been developed to achieve *operando* measurement of intra-pellet compositions. In the methanol-pentane system, for which there is a significant difference in diffusion coefficient between phases, a diffusion-based NMR method has been developed to discriminate and measure the intra-pellet liquid and gas compositions. These data give insight into the adsorption equilibrium and VLE in pores. In the 1-octene hydrogenation system, for which there is no significant difference in diffusion coefficients between species in the inter- or intra-pellet space, a method based on NMR lineshape has been developed to measure the intra-pellet compositions along the length of reactor during 1-octene hydrogenation and reveals the switch between hydrogenation and isomerisation along the reactor.

### References

- [1] Q. Zheng, F.J.R. Abegao, A.J. Sederman, L.F. Gladden, Chem. Eng. Sci. 171 (2017) 614–624.

### Keywords

*Operando* measurement; intra-pellet composition; NMR

# Qingyuan Zheng, PhD

Address: Department of Chemical Engineering and  
Biotechnology, Cambridge CB3 0AS, UK

Email: qz240@cam.ac.uk, Phone: +44 7449023310  
Nationality: Chinese

---

## Education

2011 – 2016 **PhD in Chemical Engineering, University of Cambridge, UK**  
2007 – 2011 **Bachelor of Engineering, Tsinghua University, P.R.China**

---

## Research Experience

- 2016 – present **Postdoctoral Research Associate – Magnetic Resonance Research Centre, University of Cambridge, funded by Royal Dutch Shell**
- Project: Development and application of advanced magnetic resonance techniques to the optimisation of Fischer-Tropsch synthesis process.
  - Obtained experimental evidence of water condensation in catalyst pores saturated by wax at reaction conditions and achieved for the first time *operando* measurement of the amount of intra-pellet water and the molecular dynamics of water and wax molecules.
  - Obtained insight into the mechanism of the formation of water-wax emulsion in porous media at reaction conditions. Studied the effect of temperature and material pore size on the water-hydrocarbon emulsion in porous media.
  - Conducted the first *operando* magnetic resonance study of Fischer-Tropsch reaction on a pilot-scale fixed-bed reactor rig and achieved temporally- and spatially-resolved measurement of the amount and diffusion coefficient of products.
  - Development of NMR techniques for the *operando* measurement of product distribution of the reaction.
- 2011 – 2016 **PhD in Chemical Engineering – University of Cambridge, funded by Qatar National Research Fund and Trinity College, Cambridge**
- Project: Magnetic resonance study of intra-pellet phenomena in porous media and the coupling with reactor hydrodynamics.
  - Achieved *operando* mapping of intra-pellet compositions along a trickle-bed reactor during 1-octene hydrogenation and direct measurement of the liquid-solid mass transfer coefficient during reaction by developing a novel method combining advanced regression modelling and NMR spectroscopy.
  - Obtained insight into the phase behaviour of the methanol-pentane system in a porous silica at high temperature and pressure using multiple NMR techniques. Developed a novel analysis method that allows *operando* measurement of the relative amounts and compositions of intra-pellet liquid and gas. Obtained the diffusivities and surface interaction strengths of different chemicals during the process.
  - Achieved chemically-resolved measurement of the surface interaction strength of linear alkanes, primary alcohols and their mixtures in liquid-saturated pores of a Fischer-Tropsch catalyst.
  - Obtained experimental evidence of the trickle-to-pulse transition mechanism in a trickle bed using an ultra-fast MRI imaging technique.
- 2010 – 2011 **Bachelor of Engineering, dissertation project – Tsinghua University, P.R.China**
- Kinetics study of the catalytic de-nitrification reaction; obtained the influence of reactant concentrations and reaction temperature, and determined kinetic equation.
- 

## Publications

- **Zheng, Q.**, Abegao, F.J.R., Sederman, A.J., Gladden, L.F., 2017. *Operando* determination of the liquid-solid mass transfer coefficient during 1-octene hydrogenation. Chem. Eng. Sci. 171 614-624. (featured cover article)
- **Zheng, Q.**, Brown, J.L., Sederman, A.J., Mantle, M.D., Gladden, L.F., Water phase behaviour in a n-octacosane-saturated silica at temperature and pressure relevant to Fischer-Tropsch synthesis. *Submitting*

- **Zheng, Q.**, Baker, L., Gladden, L.F., Sederman, A.J., Magnetic resonance study of the phase behaviour of the methanol-pentane system in a porous silica: Single-component phase behaviour. *submitting*
  - **Zheng, Q.**, Baker, L., Gladden, L.F., Sederman, A.J., Magnetic resonance study of the phase behaviour of the methanol-pentane system in a porous silica: Binary mixture phase behaviour. *Submitting*
- 
- 

## Presentations

- "Optimisation of heterogeneous catalytic processes using magnetic resonance". Seminar, RIPP, China Sinopec, 2016. Invited talk.
  - "NMR measurement of the adsorption of hydrocarbons and alcohols on Ru/Al<sub>2</sub>O<sub>3</sub> catalysts". CUEN Annual Conference, Cambridge, UK, 2014. Poster (best poster prize).
  - "Investigation of trickle-to-pulse transition mechanism in trickle-bed reactors using MRI". Graduate Conference, Department of Chemical Engineering and Biotechnology, Cambridge, UK, 2014. Talk.
  - "Measurement of intra-particle chemical compositions in a trickle-bed reactor using a MRI-PLSR method". 12<sup>th</sup> ICMRM Conference, Cambridge, UK, 2013. Poster.
- 
- 

## Awards

2014	<b>Best poster prize, CUEN Annual Conference</b>
2011	<b>PhD research award, Trinity College, Cambridge</b>
2007	<b>Outstanding graduate award, Qinzhou Second High School, Guangxi, P.R. China</b>

---

---

## Research Skills

### Reaction and process engineering

- *In situ* conversion and selectivity measurement; Reactor hydrodynamics; Reaction kinetics; Laboratory- and pilot-scale reactor rig design; Pilot-scale reactor control

### Heterogeneous catalysis and material science

- Diffusion and molecular dynamics in porous media; Fluid phase equilibrium in porous media; surface adsorption strength measurement; Adsorption isotherm measurement; Temperature programmed desorption (TPD); Catalyst preparation.

### Magnetic resonance and analytical techniques

- <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy; 1D and 2D NMR relaxation measurements; NMR PFG diffusion measurement; MRI imaging. GC.
- 
- 

## Additional Skills

### Project management

- Planned and managed postdoc and PhD research projects.
- Lead in the Shell funded Fischer-Tropsch project team that comprises two PhD students.

### Collaboration and team working

- Collaborate and work with industry collaborators in postdoc and PhD projects.
- Daily work in a team with two PhD students in the postdoc projects.

### Supervision

- Supervise two PhD students in their research projects.

### Communication

- Write journal papers, PhD thesis and progress reports regularly.
- Oral presentation in conferences, department seminars and group meetings.