# *In situ* $^{13}$C DEPT-MRI as a tool to spatially resolve chemical conversion and selectivity of a heterogeneous catalytic reaction occurring in a fixed-bed reactor†

**Belinda S. Akpa, Michael D. Mantle, Andrew J. Sederman and Lynn F. Gladden***

*Received (in Cambridge, UK) 3rd February 2005, Accepted 16th March 2005*
*First published as an Advance Article on the web 11th April 2005*
**DOI: 10.1039/b501698c**

**The distortionless enhancement by polarisation transfer (DEPT) nuclear magnetic resonance (NMR) technique, combined with magnetic resonance imaging (MRI), has been used to provide the first *in situ* spatially-resolved and quantitative measurement of chemical conversion and selectivity within a fixed-bed reactor using natural abundance $^{13}$C NMR.**

Chemical mapping within optically opaque three-dimensional (3D) systems is of generic importance in the chemical and biological sciences. Further, it is often the case that it is a species in relatively low concentration that is of interest, thereby requiring an imaging capability that can identify particular molecular species within a large reservoir of other species. Our interest is in understanding the coupling of hydrodynamics and reaction kinetics in porous media and, in particular, fixed-bed catalytic reactors. Here, we demonstrate how conventional MRI combined with a magnetic resonance polarisation enhancement technique can be used to spatially resolve both the conversion and selectivity characterising a heterogeneous catalytic reaction occurring within a fixed-bed reactor. This is achieved *without* the need to isotopically enrich with $^{13}$C, and thus is a cost-effective method that may be used in routine applications. The technique is illustrated with reference to the competitive etherification and hydration reactions of 2-methyl-2-butene (2M2B) (ESI†) occurring within a fixed bed of $H^+$ ion-exchange resin; this is a reaction of industrial significance with respect to the production of oxygenates for use as gasoline additives.[1] The products of the etherification and hydration reactions are *tert*-amyl methyl ether (TAME) and *tert*-amyl alcohol (TAOH) respectively.

Magnetic resonance techniques have already met with considerable success in studying catalyst systems at size-scales up to that of individual catalyst particles (~2–5 mm). NMR spectroscopy is a well-established tool for the *in situ* study of catalytic processes for the purposes of understanding the nature of active sites and surface species. More recently, magnetic resonance techniques have provided insight into mass transport processes and carbon laydown within catalyst particles.[2,3] However, in industrial-scale applications the catalyst particles will, typically, be packed within fixed-bed reactors. Magnetic resonance flow imaging has revealed significant heterogeneity in the flow field within such reactors. For example, in some regions of the inter-particle space, fluid flow may be an order of magnitude faster than in other regions of the bed.[4] Therefore it is important to understand how this heterogeneity in flow pattern within the reactor influences chemical conversion and selectivity within the reactor. While illustrated here with respect to a small-scale fixed-bed reactor, the issue of heterogeneity in hydrodynamics and the impact of this on catalyst effectiveness and selectivity is generic to most, if not all, reactor designs from large scale reactors down to microchannel reactors; all of these being topics of current interest within our group.

In studying a hydrocarbon reaction using NMR spectroscopy, two approaches are typically used, namely $^1$H or $^{13}$C observation. Whenever possible, observation of the $^1$H nucleus is the method of choice thereby exploiting the 99.9% natural abundance and inherent NMR sensitivity of the $^1$H nucleus. Whenever spatially resolving a signal, the success of the experiment depends on the signal-to-noise available, as this will determine the spatial resolution that can be obtained. However, the disadvantage of using $^1$H observation is that the $^1$H nucleus has a relatively narrow chemical shift range which, combined with the large number of $^1$H resonances present in a typical spectrum of a hydrocarbon reaction and the broadening of these resonances as a result of decreased spin–spin relaxation times arising from the high liquid–solid interfacial area within the sample, gives rise to a large number of overlapping resonances making spectral assignment and the quantification of peak areas difficult. The alternative approach is to observe the $^{13}$C nucleus. By moving to $^{13}$C observation, spectral assignment is easier because the $^{13}$C nucleus has a much wider chemical shift range than $^1$H, thereby reducing the number of overlapping peaks. Consequently, individual spectral peaks should be more readily resolved. However, given that the natural abundance of the $^{13}$C nucleus is only 1.07% and its NMR sensitivity is lower than that of $^1$H by a factor of 5870, there is considerable loss of signal-to-noise when employing $^{13}$C as opposed to $^1$H observation. In solid state NMR, which typically uses small, closed sample volumes ($\sim$1 cm$^3$), this decrease in sensitivity and natural abundance is addressed by isotopically enriching the species of interest with $^{13}$C. However, in studying chemical composition within a reactor operating under conditions of continuous flow, this approach is prohibitively expensive.

To date, there have only been two reports of spatially mapping conversion within a catalytic reactor. Whilst successful in developing this field of research, both illustrate the limitations of using $^1$H observation as a generic approach. In the first report, we used volume selective magnetic resonance spectroscopy to quantify the conversion of an esterification reaction occurring within a fixed bed of ion-exchange resin.[5] Conversion was quantified by the chemical shift of the $^1$H resonance of the OH groups present in the

† Electronic supplementary information (ESI) available: competitive reactions of 2M2B. See http://www.rsc.org/suppdata/cc/b5/b501698c/

*gladden@cheng.cam.ac.uk

reaction mixture within the inter-particle space of the bed. This approach can only be used for reactions in which the $^1$H spectrum is relatively simple, such that assignment of changes in chemical shift can be related unambiguously to changes in chemical conversion. More recently, Koptyug *et al.*[6] used $^1$H NMR to produce spatially resolved spectra within a 2D slice section along the axial direction of a fixed bed of $Pd/Al_2O_3$ (1% by weight) catalyst pellets. The reaction considered was that of the hydrogenation of α-methylstyrene to cumene. The spectra show evidence of changes in chemical composition along the length of the bed, but conversion was not quantified, most likely due to problems in deconvolving the $^1$H resonances associated with the reactant and product species. Thus the aim of the present work was to implement a spatially resolved magnetic resonance imaging technique, which (i) provides sufficient signal-to-noise that spatial resolution in the measurement can be obtained; and (ii) employs $^{13}$C observation such that the amount of reactant and product species, and hence conversion and selectivity, at specific locations can be quantified. Further, (i) and (ii) are to be achieved without need for isotopic enrichment of $^{13}$C. We report here the first application of an integrated NMR/MRI experiment for the *in situ* monitoring of a heterogeneous catalytic reaction, achieved by observing the $^{13}$C nucleus at natural abundance.

Imaging of conversion within the fixed bed was achieved using a proton-decoupled $^{13}$C distortionless enhancement by polarization transfer (DEPT) spectroscopy pulse sequence[7] integrated into an imaging sequence (Fig. 1). This hybrid imaging and spectroscopy scheme was first proposed by Yeung and Swanson[8] who demonstrated its use in application to a liquid phantom comprising ethanol, ethylene glycol and acetone. In our work, the technique has been implemented for the first time to study, quantitatively, reaction in a fixed bed. Fig. 2 shows $^{13}$C DEPT-MRI spectra obtained from two liquid mixtures comprising the reactant and product species present in the reaction to be studied in the reactor environment. The conversion, $X$, and selectivity to TAME, $S$, corresponding to each mixture composition is quantified as follows. Conversion is measured by taking the ratio of the peak areas corresponding to the products and reactants. The spectral resonances of the same carbon group need to be compared between species since the degree of polarisation transfer (*i.e.* signal enhancement) is dependent on the chemical environment of each specific carbon atom. In this case the $CH_3$ resonances have been compared; for the products TAME and TAOH these occur at ~8 ppm ($CH_3$ resonances for TAME and TAOH occur at 7.8 and 8.7 ppm respectively), while those of the reactant 2M2B occur at 13.4, 17.3 and 25.7 ppm. All chemical shifts are quoted with respect to the $^{13}$C resonance of tetramethylsilane (TMS).

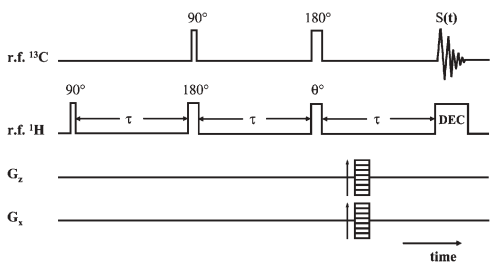


**Fig. 1** $^{13}$C DEPT-MRI pulse sequence. The signal is acquired under conditions of $^1$H decoupling.

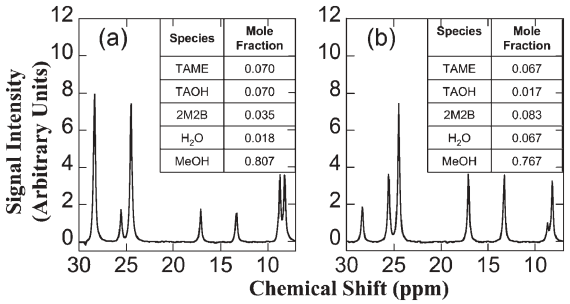


**Fig. 2** $^{13}$C DEPT-MRI spectra confirming the quantitative measurement of liquid mixture composition. Spectra are shown for mixture compositions simulating conversions of 2M2B and selectivities to TAME of (a) $X$ = 80%, $S$ = 50%, and (b) $X$ = 50%, $S$ = 80%.

Selectivity to TAME is quantified by comparing the intensities of the $CH_3$ resonances of TAME and TAOH which occur at 24.1 and 28.7 ppm, respectively. For example, in Fig. 2a, TAME and TAOH have similar peak areas indicating equal amounts of the two products (*i.e.* $S$ = 50%), while the combined area of the two product peaks (each representing two C atoms per molecule) is ~8 times that of either 2M2B peak (13.4 and 17.3 ppm), consistent with $X$ = 80%. Mixture compositions determined from the spectra were accurate to 5%.

The reaction studied using the integrated $^{13}$C DEPT-MRI pulse sequence was the competitive etherification and hydration reaction of 2M2B occurring within a fixed-bed reactor. The reactants used were methanol (>99%), 2-methyl-2-butene (>99%), and water. The catalyst used was Amberlyst® 15 (Rohm & Haas), an ion-exchange resin in the form of beads of diameter 600–850 μm. A randomly packed bed was formed by pouring ~20 g of wet catalyst into a methanol-filled column of inner diameter and length 15 mm and 15 cm respectively. A liquid of molar composition 2:10:1 (2M2B:methanol:water) was fed to the bottom of the bed at a rate of 0.02 ml min$^{-1}$. Methanol was used in excess to ensure the formation of a single liquid phase. The reaction temperature was maintained at 40 °C. The reaction conditions were consistent with those reported by earlier workers.[1] All $^{13}$C DEPT-MRI experiments were performed using a Bruker Biospin DMX-300 NMR spectrometer with a 7.07 T vertical magnet, equipped with shielded gradient coils, and providing a maximum gradient strength of 100 G cm$^{-1}$. A birdcage radio-frequency (r.f.) coil of diameter 20 mm, dual-tuned to 300.1 MHz and 75.5 MHz for the $^1$H and $^{13}$C resonances respectively, was used. The duration of the $^1$H and $^{13}$C 90° pulses were 32 μs and 30 μs respectively. The phase gradients were of duration 462 μs and were ramped to a maximum value of 4.09 G cm$^{-1}$ and 2.73 G cm$^{-1}$ in 16 increments and 8 increments respectively. In-plane spatial resolution was 2.5 mm ($z$) × 3.75 mm ($x$). 64 averages were acquired with a recycle delay of 7 s, yielding a total acquisition time of 16 hours. A schematic showing an image of the bed and the location of 3D spectra recorded from within the bed is shown in Fig. 3.

Typical results are shown in Fig. 4. The data have been recorded from a vertical section through the centre of the fixed bed [*i.e.* column (iii) in Fig. 3]. The average conversion and selectivity calculated from the spectra acquired from columns (i) to (v), at each axial location identified in Fig. 3, are shown in Fig. 5. Over a 1.5 cm height of the bed, conversion is found to increase by ~30%,

 

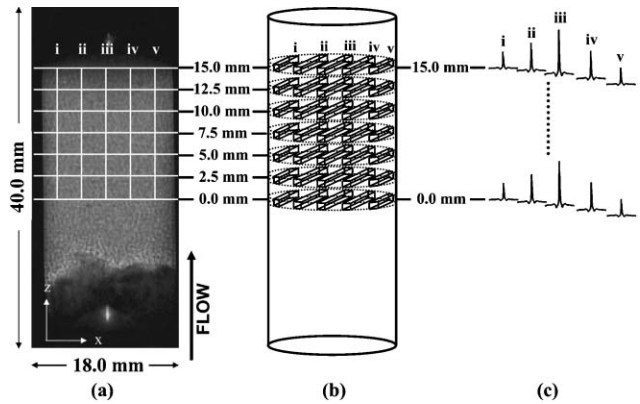


**Fig. 3** Schematic showing how the double-phase encoded $^{13}$C DEPT-MRI pulse sequence achieves both spatial and spectral resolution within the reactor. (a) A $^{1}$H 2D spin-echo image taken through the reactor, overlaid with a grid showing the location of the two orthogonal phase encoded planes ($z$ and $x$). In-plane spatial resolution is 156 μm ($z$) × 141 μm ($x$) for a 3 mm slice thickness. The centre of each volume from which the data have been acquired is identified by the intersection of the white lines. (b) The corresponding real space volume elements. The individual volume elements have been separated for clarity but actually form a continuous array. (c) $^{13}$C NMR spectra associated with the volume elements shown in (b). The decreasing signal intensity towards the walls of the bed arises from the smaller volumes from which the data are sampled.

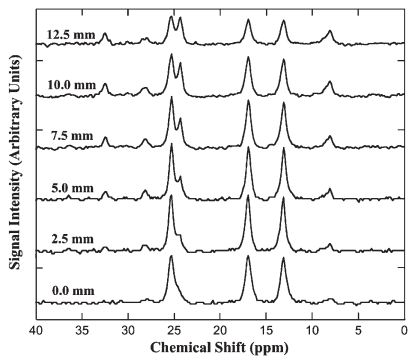


**Fig. 4** Spatially resolved $^{13}$C DEPT-MRI spectra recorded for the competitive etherification and hydration reactions of 2M2B to TAME and TAOH respectively. Spectra are recorded at different heights within the bed (see Fig. 3).

while selectivity lies in the range 75–80%. At any given axial position, both conversion and selectivity also vary across the transverse plane. Fig. 6 shows the conversion and selectivity observed within five locations across the bed [columns (i–v) in Fig. 3] at three different axial locations along the bed. It is clearly seen that the conversion can vary by ~15% across a given transverse section, at a given axial location. In particular, the relatively low conversions in columns (i) and (v) in Fig. 6b and c are consistent with the faster flow rates, and hence reduced feed-catalyst contact time, often observed towards the walls of fixed-bed reactors. We are currently applying $^{13}$C DEPT-MRI to study a range of reactions, including some occurring over supported-metal catalysts, in combination with spatially resolved imaging studies of

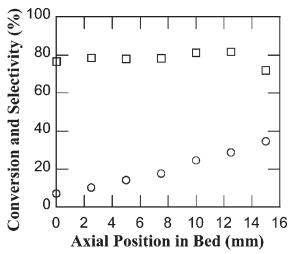


**Fig. 5** Conversion (○) and selectivity (□) as a function of axial position in the bed (averaged over the transverse plane). Decreasing signal-to-noise towards the limit of the field-of-view introduces greater error in the measurements recorded at 15 mm.

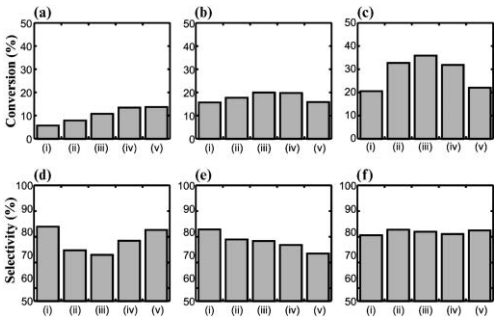


**Fig. 6** Conversion and selectivity, as determined from $^{13}$C DEPT-MRI, are shown at three axial locations along the length of the bed. At each location, conversion (a–c) and selectivity (d–f) are also spatially resolved at 5 different locations in the $x$-direction across the bed. The axial locations are those corresponding to 2.5 mm (a, d), 7.5 mm (b, e), and 12.5 mm (c, f), as identified in Fig. 3.

the flow regimes within the same reactors. This method offers the opportunity to gain substantial new insights into the coupling of hydrodynamics and chemical kinetics within catalytic reactors.

LFG gratefully acknowledges EPSRC for financial support.

**Belinda S. Akpa, Michael D. Mantle, Andrew J. Sederman and Lynn F. Gladden***
*Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3RA.*
*E-mail: gladden@cheng.cam.ac.uk; Fax: +44 (0)1223 334796; Tel: +44 (0)1223 334762*

## Notes and references

1 J. A. Linnekoski, A. O. I. Krause and L. K. Struckmann, *Appl. Catal., A*, 1998, **170**, 117.
2 M. P. Hollewand and L. F. Gladden, *Chem. Eng. Sci.*, 1995, **50**, 309.
3 K. Y. Cheah, P. Chiaranussati, M. P. Hollewand and L. F. Gladden, *Appl. Catal., A*, 1994, **115**, 147.
4 A. J. Sederman, M. L. Johns, P. Alexander and L. F. Gladden, *Chem. Eng. Sci.*, 1998, **53**, 2117.
5 E. H. L. Yuen, A. J. Sederman and L. F. Gladden, *Appl. Catal., A*, 2002, **232**, 29.
6 I. V. Koptyug, A. A. Lysova, A. V. Kulikov, V. A. Kirilov, V. N. Parmon and R. Z. Sagdeev, *Appl. Catal., A*, 2004, **267**, 143.
7 M. R. Bendall, D. M. Doddrell and D. T. Pegg, *J. Am. Chem. Soc.*, 1981, **103**, 4603.
8 H. N. Yeung and S. D. Swanson, *J. Magn. Reson.*, 1989, **83**, 183.