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In situ MRI of the structure and function of multiphase catalytic reactors

Igor V. Koptyug [a,*], Anna A. Lysova [a], Renad Z. Sagdeev [a], Valery A. Kirillov [b], Alexander V. Kulikov [b], Valentin N. Parmon [b]

[a] *International Tomography Center, Institutskaya St. 3A, Novosibirsk 630090, Russia*
[b] *Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia*

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Abstract

NMR imaging (MRI) was used to study the distribution of the liquid phase in an operating trickle bed reactor using hydrogenation of α-methylstyrene or *n*-octene-1 as representative examples. In a single pellet reactor, the existence of oscillating regimes under unchanged external conditions was shown. The experiments with packed beds have demonstrated the non-uniform distribution of the liquid phase over the bed, the presence of partially liquid-filled or completely dry catalyst particles in the operating reactor, and the existence of liquid phase transport between liquid-filled and dry catalyst particles. Detection of spatially resolved NMR spectra was used to characterize chemical conversion variations within the operating reactor. Preliminary MRI results for an operating monolithic reactor were obtained. It was found that MRI can be used to directly image solid materials using NMR signal detection of nuclei other than ^{1}H. In particular, imaging of alumina using ^{27}Al NMR signal appears highly promising for the development of novel MRI applications in chemical engineering and catalysis, including spatially resolved NMR thermometry.

Keywords: Trickle bed reactor; Hydrogenation; Monolithic catalyst; In situ MRI

1. Introduction

A variety of modern imaging techniques are employed in chemical engineering and catalytic research [1]. The majority of these techniques, however, can yield only structure-related information and can provide little insight into the functional behavior of an operating reactor. In this respect, NMR imaging (MRI) is a unique technique due to its ability to provide spatially resolved maps of a variety of essential parameters characterizing an operating reactor based on the appropriate choice of image contrast mechanisms [2–4]. Until recently, in chemical and process engineering MRI was predominantly used to characterize mass transport processes under non-reactive conditions [5,6]. Direct visualization of multiphase catalytic processes is a relatively new modality of MRI, which nevertheless appears highly promising. In particular, it has been demonstrated already that MRI can be successfully employed to characterize liquid phase distribution and reactant-to-product conversion in catalyst pellets and granular catalyst beds within an operating trickle bed reactor [7–12]. There is no doubt, however, that further development of MRI applications in the field of chemical engineering and catalysis is needed and that future progress in this field will allow one to obtain an unprecedented amount of detail about physicochemical processes taking place at different length scales in an operating multi-phase reactor. Some recent developments in this field are presented below.

2. Experimental

The catalysts used contained 0.1% Mn and 1% Pd by weight on the γ-Al_2O_3 supports shaped as cylinders 4.5 mm

* Corresponding author. Tel.: +7 3833 333 561; fax: +7 3833 331 399.
E-mail address: koptyug@tomo.nsc.ru (I.V. Koptyug).

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in diameter and 12 mm long, or beads of 1, 2–3 or 4.2 mm in diameter. Before any hydrogenation experiment, individual catalyst pellets were activated in a mixed H_2-air stream with excess of hydrogen. For 1 mm and 2–3 mm beads, the catalyst bed was activated for 30 min in H_2 stream at 450 °C followed by cooling to room temperature in a stream of He. The bed of 4.2 mm beads was activated in a H_2-air stream with excess of hydrogen, then heated to 450 °C in a stream of He, and then cooled back to room temperature without interrupting He stream. After activation, the catalyst was loaded into the reactor residing inside the NMR magnet. Catalyst beds were often placed on a layer of inert beads (Mn/γ-Al_2O_3) of the same size.

All imaging experiments were performed on a Bruker Avance DRX 300 MHz wide bore spectrometer equipped with imaging accessories, at 300.13 MHz (^{1}H) or 78.2 MHz (^{27}Al). Two-dimensional images were obtained using the 2-pulse spin-echo sequence α–τ–2α–τ-echo. All 2D images of individual catalyst pellets and transverse images of catalyst beds were obtained with 230 μm × 140 μm spatial resolution, while for axial images of the bed it was 230 μm × 310 μm. The rapid 3D imaging of the operating catalyst bed or monolith was performed using the multi-echo pulse sequence, with each 3D image acquired within ca. 1 min.

The solids imaging experiments were performed using the α–τ–2α–τ-echo sequence, with $\tau \approx 300$ μs and the nominal flip angle $\alpha = 90°/(I+1/2)$. The two spatial coordinates were phase encoded by an independent stepwise variation of two pulsed transverse gradients. A field of view FOV = $(9.2\ \text{mm})^2$ was imaged with a spatial resolution of $(288\ \mu\text{m})^2$ without slice selection.

3. Results and discussion

For our studies, hydrogenation of unsaturated hydrocarbons, such as α-methylstyrene (AMS), *n*-heptene-1 or *n*-octene-1 on a Pt/γ-Al_2O_3 or Pd/γ-Al_2O_3 catalyst at elevated temperatures has been chosen both for its importance in industry and a wide use as a model reaction. For these studies, an NMR-compatible reactor has been built which enables us to perform catalytic hydrogenation at temperatures up to 100 °C without damaging the spectrometer hardware [10–12]. Despite the limited size of the sensitive volume (1 cm in diameter, ca. 3–4 cm long), temperature rises of the catalyst up to 250 °C were observed in some experiments.

In order to perform MRI of dynamic processes, image acquisition time should be relatively short. In our recent studies, it has been reduced from 4 to 5 min down to 0.5 min by impregnating catalyst pellets with a small amount of paramagnetic Mn. The latter reduces spin-lattice relaxation time of nuclear spins and allows one to reduce imaging time. As a result, it became possible to detect 3–4 two-dimensional (2D) slices through the granular bed within ca. 30 s. This has proven to be a significant step forward in such applications. In particular, a number of interesting dynamic processes have been visualized. In a single pellet reactor, the existence of oscillating regimes under unchanged external conditions has been demonstrated. The radial or axial reciprocating motion of the liquid front inside the catalyst pellet partially filled with the reactant has been visualized in the course of AMS hydrogenation reaction. These pulsations were accompanied by pellet temperature oscillations, revealing a complex interaction of mass and heat transport processes with the chemical transformation [12]. Radial pulsations are observed for large liquid contents of the pellet and resemble particle ignition due to autocatalytic acceleration of the exothermic hydrogenation process. It was possible to model the oscillating behavior using a set of coupled differential equations which take due account of heat and mass transfer, phase transitions and chemical transformation [13].

Using the imaging time reduction approach described above, a number of studies have been performed on a regularly packed granular catalyst bed comprising uniform catalyst beads a few millimeters in diameter. Liquid AMS was supplied to the top of the packing through a thin capillary. All experiments have demonstrated that despite the regular character of the catalyst beads packing, the distribution of the liquid phase in the bed is highly non-uniform, and that the steady state distribution of liquid within the bed changes if the supply of the liquid reactant to the top of the bed is interrupted and then turned on again. For larger beads (4–5 mm), images have revealed the existence of partially filled or completely dry pellets in the operating reactor. As an example, Fig. 1 demonstrates sequential ignition of individual catalyst beads constituting the bed as the supply rate of liquid reactant is progressively reduced. In some experiments it has been observed that after ignition of one of the beads in the bed, it can remain almost dry throughout the rest of the experiment, sipping liquid reactant from its liquid-filled neighbors. Presumably, such beads act as ''microreactors'' and the liquid reactant they imbibe evaporates readily and rapidly undergoes gas phase hydrogenation on the dry exposed surface of the catalyst.

Our most recent efforts have addressed several issues essential for the further development of the applications of the versatile MRI toolkit in chemical engineering and heterogeneous catalysis. First, further development and implementation of rapid imaging strategies has been carried out. As a result, a complete 3D image of the granular bed with sub-millimeter spatial resolution can now be obtained within 20–30 s. Furthermore, while in the previous studies the liquid in the inter-pellet voids could not have been observed, it is now possible to visualize separately the inter- and intra-pellet liquid within the same image acquisition time. An example of the experimental results is presented in Fig. 2. The two images shown represent the same 2D plane of a set of complete 3D images detected in the experiment. They reflect the distribution of the liquid phase in the

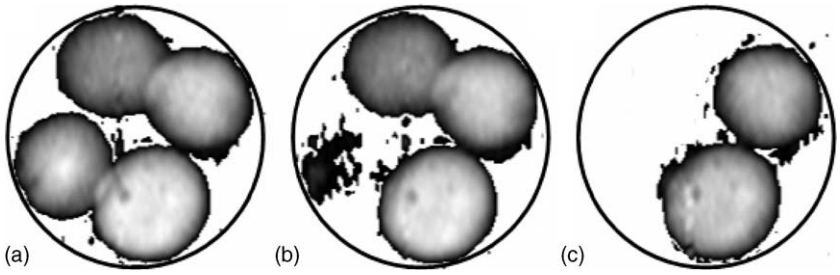

Fig. 1. Distribution of the liquid phase in a regularly packed bed of 4.2 mm catalyst beads (1% Pd/γ-Al_2O_3) during AMS hydrogenation. Hydrogen gas temperature, 91 °C; flow rate, 39.7 cm^3/s. Images were detected for a progressively decreasing AMS supply rate: 2.07×10^{-1} g/s (a), 1.13×10^{-1} g/s (b), 3.23×10^{-2} g/s (c). Lighter shades of gray correspond to higher liquid contents. Dry catalyst pellets are not observable by ^{1}H MRI and therefore disappear from the image.

operating trickle bed reactor for different liquid reactant supply rates. Analysis of the complete 3D images has revealed that even at the highest reactant supply rates used in these experiments, the inter-particle voids are not filled with the liquid. At the same time, along with the liquid within the catalyst beads, some liquid is clearly present near the contacts of the beads with the reactor walls and with each other. Therefore, it appears that transport of the liquid phase proceeds mostly as film flow over the surface of the catalyst particles. These developments make it possible to observe rapid dynamic processes in the operating reactor and thus provide an unprecedented access to the information on the coupling of mass transport and phase transitions with the chemical reaction itself. The results obtained on the operating trickle bed reactors shed new light on the mechanisms of the development of critical phenomena (such as hot spots, temperature oscillations, reactor runaway). In particular, the results obtained seem to indicate that phase equilibrium during an exothermic reaction can be violated locally making the reactor prone to runaway.

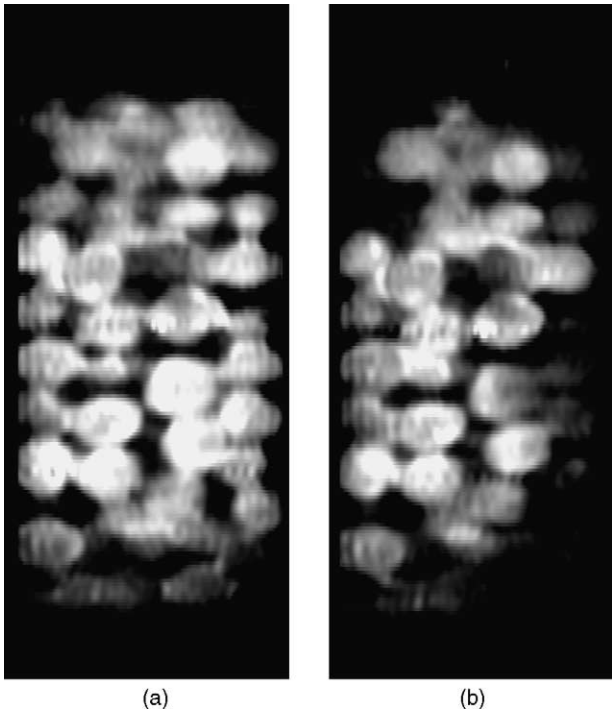

Fig. 2. Distribution of the liquid phase in a bed of 2–3 mm catalyst beads (1% Pd/γ-Al_2O_3) during *n*-octene-1 hydrogenation. Hydrogen gas temperature, 79 °C; flow rate, 36 cm^3/s; octene supply rate: 7.5×10^{-2} g/s (a), 5.16×10^{-2} g/s (b). Lighter shades of gray correspond to higher liquid contents.

Since NMR is a spectroscopic technique, combining NMR and MRI approaches it is possible to obtain spatially resolved NMR spectra and thus to evaluate local degree of chemical conversion. Despite the significant broadening of the NMR spectra of liquids permeating porous solids, NMR spectra obtained for each voxel (volume element) of an image can still provide at least semi-quantitative information about the local chemical conversion in an operating reactor, especially if the reaction is carried out at elevated temperatures. In particular, in the studies of AMS hydrogenation, the relative amounts of AMS and reaction product cumene have been mapped during the reaction inside the trickle bed reactor, demonstrating both axial and radial conversion variations within it [12].

At present we are extending our MRI studies of an operating multiphase reactor to other types of reactions and reactor types. Fig. 3 exemplifies the preliminary study of *n*-octene-1 hydrogenation in a monolithic reactor using a Pd catalyst supported on an alumina washcoated cordierite monolith. The distribution of the liquid phase in one row of the monolith channels is clearly visible in the image. In this experiment, liquid substrate was predominantly supplied to the top of the central channel which carries most of the liquid and gas flow. Nevertheless, other channels contain noticeable amounts of liquid near the lower (outflow) edge of the monolith. In these experiments, the 3D imaging approach developed for the imaging of liquid in a trickle bed was employed, leading to relatively long image acquisition times (30 s) and yielding time averaged images, which can be inappropriate for certain flow regimes (e.g., bubble-train flow). It should be noted, however, that imaging of the bulk liquid can be done much faster than imaging of the liquid permeating porous solids. Future progress in this field will be based on the implementation of rapid imaging techniques for the elucidation of liquid transport and spatially resolved

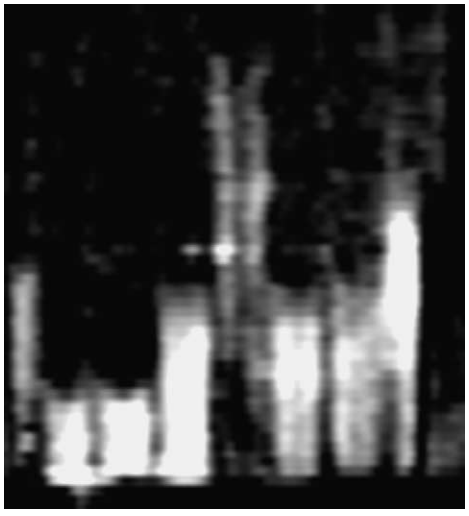

Fig. 3. Distribution of the liquid phase in the channels of alumina wash-coated cordierite monolith (400 cpsi) containing 1 wt% Pd detected during *n*-octene-1 hydrogenation. H_2 temperature, 79 °C; flow rate, 36 cm^3/s; octene supply rate, 5.16×10^{-2} g/s. A 2D plane is shown which was selected from a complete 3D image and is parallel to the axes of the monolith channels. Lighter shades of gray correspond to higher liquid contents.

conversion of reactant into product in an operating monolithic multiphase reactor.

Most of the MRI studies reported to date, including those presented above, are based on the detection of ^{1}H NMR signal in the liquid phase. At the same time, the ability of NMR spectroscopy to study solid materials as well as to detect magnetic nuclei other than ^{1}H is well known and appreciated in chemical research. While MRI of ''soft'' solids, such as polymers and elastomers is a well developed area of research, MRI of rigid solids is seldom done and is almost inevitably associated with the use of specialized solid state NMR hardware, sophisticated pulse sequences and very large magnetic field gradients. This implies that imaging of rigid solids cannot be performed on commercially available MRI instruments intended for the imaging of liquids and thus prevents the solids imaging from becoming a routine application. If this obstacle could be removed, it would boost the interest in the MRI of rigid solids and would eventually lead to the development of a wide range of novel applications of MRI in chemical engineering and catalysis. Somewhat to our surprise, our results demonstrate that it can be done relatively easily.

Since the catalysts used in the reactions described above use alumina supports, we first turned our attention to the ^{27}Al NMR signal of alumina. As a representative example, Fig. 4 shows a 2D image of a fragment of an alumina monolith (100 cpsi) together with a picture taken with a digital camera for comparison. The fact that the image was obtained in about 15 min on a commercial Bruker microimaging instrument using a simple 2-pulse spin-echo sequence is quite encouraging. The ^{27}Al nucleus thus appears to be very promising for catalytic applications owing to the widespread use of alumina and other aluminum-containing materials (cordierite, glass, etc.) as catalysts, catalyst supports and structural elements of catalytic reactors. The results shown in Fig. 4 and imaging of other aluminum-containing materials (alumina beads and pellets, cordierite monoliths, glass) [14,15] clearly demonstrate the possibility to use ^{27}Al MRI for structure visualization of catalyst beds and other reactor elements. Besides, we were able to demonstrate that a substantial progress in MRI of rigid solids can be achieved based on the detection of the NMR signal of other nuclei (^{7}Li, ^{11}B, ^{23}Na, ^{29}Si, ^{31}P and ^{51}V) thereby providing means for the imaging of various solid samples.

It should be stressed, however, that future applications of solids imaging are likely to extend far beyond simple structure evaluation since the major advantage of MRI is its ability to provide parameter images and thus to yield spatially resolved maps characterizing various properties of a reactor and processes within it. In particular, one of the issues of paramount importance for an operating catalytic reactor is that of heat transport. The existing approaches to NMR thermometry work well when spatially resolved temperature maps of living organisms are detected. However, they are based on the detection of the temperature dependent ^{1}H NMR signal of the liquid phase. Therefore,

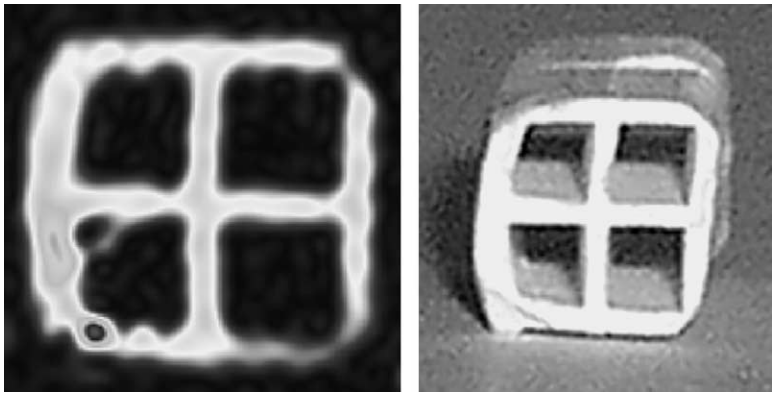

Fig. 4. Two-dimensional image (left) of a fragment of alumina monolith (100 cpsi) shown on the right. The image was detected using the ^{27}Al NMR signal within 15 min of acquisition time.

they are not applicable to the temperature measurements in an operating multiphase catalytic reactor where the weak dependence of the NMR signal on the temperature is completely masked by the significant variation of the local liquid content. The demonstrated ability to image the solid phase of the operating reactor might finally provide access to the evaluation of local temperatures. Indeed, our preliminary experiments have shown that both signal intensity and spin-lattice relaxation time of ^{27}Al NMR signal of alumina exhibit pronounced temperature dependences [14]. Based on these developments and observations, we are currently developing an MRI based technique capable of providing spatially resolved temperature maps of an operating multiphase reactor. This technique will be employed in the future to study heat transport and hot spots formation in an operating catalytic reactor and conditions leading to reactor runaway.

4. Conclusions

Modern MRI is a powerful toolkit which can be very useful in elucidating fine details of the catalytic reactor behavior. Visualization of the liquid phase distribution in a trickle bed reactor at different lengthscales exemplified above, from individual catalyst particles to the entire bed, provides information on the degree of wetting of the catalyst, mechanisms of liquid transport within the reactor, mutual influence of the neighboring catalyst particles, local phase equilibria and local chemical conversion. Rapid imaging techniques provide access to the visualization of dynamic processes, such as catalyst particle ignition and oscillating behavior observed experimentally. Such in situ studies of the coupled heat and mass transfer, phase transitions and chemical conversion are indispensable for a detailed understanding of the reactor operation and the mechanisms of the development of critical operation regimes. Furthermore, the possibility to image solid materials demonstrated above will add new powerful tools to the MRI toolkit and will enable one not only to obtain structural information (e.g., structure of a packed bed or a reactor), but also to map temperature distributions, to study transport of the solid phase, to visualize supported catalyst preparation, and to extend the studies reported above to other types of reactions and reactors.

Acknowledgements

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