NMR imaging of gas phase hydrogenation in a packed bed flow reactor

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ABSTRACT

In situ analysis of heterogeneously catalyzed gas phase reaction systems is becoming a valuable aid to their modeling and optimization. The commonly applied methods are either invasive, do not provide spatial information or are not applicable for optically inaccessible systems. This work investigates the possibility to use NMR imaging to study gas phase reaction processes in situ, spatially resolved and non-invasively.

A multislice NMR spectroscopic imaging pulse sequence, which was optimized to realize ultrashort echo time TE, was employed to study the ethylene hydrogenation reaction in an NMR-compatible packed bed flow reactor. The catalyst bed, containing inactive γ-Al$_2$O$_3$ pellets and Pt-Al$_2$O$_3$ pellets, was subdivided into several sections in order to identify reaction zones that depend on initial conditions. Spatial mapping of the chemical composition was demonstrated on the basis of two experiments with varying initial volume flow and ethylene conversion. The inlet and outlet temperature of the catalyst bed was simultaneously detected by analyzing the spectra of inserted glycol capsules.

The resulting spatial shift of the reactive zones in both experiments could be proven by the spatially resolved concentration measurements and the temperature measurements. The locations of single active catalyst pellets were also detectable by the same measure. The quantitative results of product gas composition of both experiments were in good agreement with accompanying mass spectrometric measurements.

The results demonstrate the applicability of NMR imaging methods to investigate gas phase reaction processes and can help to establish these methods as a standard tool to map chemical transformations in gas flow reactors.

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1. Introduction

Heterogeneously catalyzed gas phase reactions have a substantial relevance for the chemical and energy industry. Prominent examples are the Sabatier reaction, the hydrogenation of alkines, the partial oxidation of alkenes or the oxidative dehydrogenation of alkanes. Due to the high potential of these reactions, performance enhancements of these processes are of high interest as even small improvements can already be economically viable [1].

A well established way to achieve significant enhancements is to optimize mass and heat transport within a catalyst bed, which are known to influence parameters like activity and selectivity drastically [2–5]. To optimize the processes within a reactor, knowledge about the inner conditions of a reactor is needed. However, techniques that provide integral information about chemical composition like online gas chromatography (GC) analysis or invasive measurements like probe thermometers, which provide a rather coarse spatial resolution at selected positions, are still state-of-the-art and are widely used to validate modeling approaches [6–8]. While these methods have clearly proven their value, methods which allow to non-invasively obtain information about temperature and chemical composition combined with high spatial and temporal resolution have gained considerable attention [9–13]. These methods are particularly suitable for the investigation of microscopic processes, such as adsorption reactions and the determination of reaction intermediates. However, the investigated reaction systems have to be optically accessible, which makes these methods not applicable when information about reaction processes within opaque environments, like porous catalyst beds, should be acquired.

Another approach to map chemical compositions and temperature, particularly in optically opaque reactors, is to apply nuclear magnetic resonance (NMR) based methods, i.e. magnetic resonance imaging (MRI), localized NMR spectroscopy (MRS) or magnetic

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resonance spectroscopic imaging (MRSI) [14,15]. These NMR based methods are not only well established and widely used diagnostic tools for medical and biomedical applications, but have also found various applications in material sciences and chemical engineering [16]. NMR based methods offer a lot of advantages compared to other methods. They are not only non-invasive, but additionally provide a whole realm of contrast mechanisms such as concentration, relaxation times, flow, diffusion, temperature or magnetization transfer. In particular, they allow to simultaneously measure parameters like chemical composition and temperature with both high spatial and temporal resolution, which is crucial to validate spatially resolved simulations of catalytic reactors.

Nowadays, suitable NMR imaging systems are widely available, although often in research facilities focusing on biomedical research, and not on material sciences or catalysis. Thus, MRI and MRSI might appear to be ideal tools to non-invasively investigate macroscopic transport processes within chemical reactors in situ. However, scientific publications on this topic are still rather rare, which is due to several reasons:

(i) A reactor designed for operation within an MRI magnet has to be made of NMR-compatible materials. The use of metals is limited, even if non-magnetic, as they would distort the static magnetic field B0 and/or screen the radio frequency (RF) field B1, thus making MRI measurements impossible. Therefore, the design of NMR compatible reactors is challenging, particularly for high temperature and high pressure.

(ii) The interaction between molecules of liquids or gases, which are to be measured, and the porous carrier material with the catalyst shortens the effective transverse relaxation time T2*. Thus the transverse magnetization decays rapidly after RF excitation, resulting in a decreased signal-to-noise ratio (SNR). Additionally, short T2* values require to apply strong and rapidly switchable B0 gradients for spatial resolution as well as optimized pulse sequences with ultrashort echo time (TE), i.e. an ultrashort delay between RF excitation and signal detection.

(iii) NMR is an inherently insensitive method with respect to SNR, e.g., as compared to mass spectrometry. This fact limits the detection of samples with low concentration of NMR active nuclei as well as the achievable spatial resolution. Solutions to this problem comprise the use of hyperpolarization [17,18] or special detection techniques such as "remote detection" [19,20].

(iv) Most of the suitable modern NMR imaging systems are available in a biomedical research environment and not in engineering departments. Considering the difficulties mentioned above and the high prices of NMR imaging systems, initial MRI or MRSI experiments for characterizing catalytic reaction will most likely require a multidisciplinary cooperation. However, this may be difficult to establish because of the considerable experimental requirements and the remaining risks of such projects.

Nevertheless, excellent work on investigating 3-phase reaction systems with MRI methods has been published, e.g., on octene hydrogenation and alpha-methylstyrene hydrogenation [21–25]. Furthermore, a method using the temperature dependence of chemical shift difference between the two signals of ethylene glycol, well known from high resolution NMR spectroscopy [26], was adapted for temperature measurements within an NMR compatible reactor [27]. Even gas phase reactions were investigated by using hyperpolarization or remote detection techniques [28–30]. Recently, an investigation of ethylene polymerization at industrial conditions in a specially designed NMR compatible reactor has been reported [31].

Along with the general requirements for investigating reaction processes by NMR based methods, the analysis of gas phase reactions provides further challenges [32,33]. The signal intensity of gases is much lower than the intensity of liquids because of the lower spin density (factor ~1000), especially at low pressure and high temperature. The spin-spin relaxation times T2 of gases are rather short, which decreases the SNR and complicates signal detection. Additionally, the short T2 and T2* relaxation times as well as the much higher diffusion constants of gases as compared to liquids hamper spatial encoding achieved by spatially selective RF pulses, phase encoding B0 gradients or readout B0 gradients.

To address these problems, this work investigates the possibilities to apply NMR based methods to heterogeneously catalyzed gas phase processes within reactors of conventional dimensions at ambient reaction conditions. It was the aim of this study to provide a methodology for observing chemical reactions and temperature changes in a rather large reactor over a longer time (typically hours) and with low flow velocity. Therefore, the conventional approach of using a standard volume RF coil for signal detection and exploiting thermal nuclear polarization was preferred, despite the attractive features of hyperpolarization and remote detection. An NMR compatible reactor was developed for use within a standard quadrature RF volume coil of 72 mm inner diameter. For simultaneously observing the chemical reaction and temperature changes within the reactor, an optimized pulse sequence for multislice ultrashort echo time MRSI was developed. As an example, the ethylene hydrogenation reaction was chosen. Measurements were performed for different flow rate and concentration ratios. The MRSI results were compared with mass spectrometric measurements of the products.

2. Experimental

2.1. Materials

For the preparation of Pt-Al$_2$O$_3$ catalyst, commercial cylindrical γ-Al$_2$O$_3$ pellets (length: ~8 mm; diameter: 3.2 mm; BET: 220 m^2/g; Alfa Aesar GmbH) were impregnated with a solution of water and Tetraammineplatinum(II)chloride hydrate (Sigma–Aldrich).

In a first step, the pore volume of the Al$_2$O$_3$ pellets was calculated by adding water step by step to the porous material. The amount of water, which could be completely adsorbed, was 40 % of the pellet mass. To get 1 wt.% homogeneously distributed Platinum on the pellet, Tetraammineplatinum(II)chloride hydrate was dissolved in the amount of water, which corresponds to the pore volume. After adding the platinum solution to the pellets, they were dried at 120 °C and calcined at 400 °C for 3 h. Before the experiments, the catalyst was activated at a gas flow of 2.5 Nl/min (H$_2$:N$_2$ 1:5) at a temperature of 400 °C for about 2 h.

2.2. Temperature measurements

To measure the temperature level during the experiments at the inlet and outlet of the catalyst bed, cylindrical glass capsules (outer diameter 3 mm; length ca. 10 mm) were manufactured, filled with ethylene glycol (99.5 % purity, Fluka) and fused. The chemical shift difference between the —OH and —CH$_2$ peaks of ethylene glycol is known to correlate well with temperature within a range of 20 °C and 140 °C [26,34]. The temperature can be expressed as a function of the chemical shift difference $\Delta\delta$ in ppm [26]:

$$T(\text{C}^\circ) = 192.85 - 101.64\,\Delta\delta. \tag{1}$$

The ethylene glycol capsules were placed in front of and behind the reactive zone of the catalyst bed surrounded by inert Al$_2$O$_3$ pellets (cf. Fig. 1) to avoid information loss by crosstalk of the ethylene glycol signal into the gas signal. Before insertion into