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Spatially Resolved NMR Thermometry of an Operating Fixed-Bed Catalytic Reactor

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The operation of a fixed-bed catalytic reactor often involves a complicated coupling of the reaction with heat and mass transport processes, therefore the techniques for the in situ studies of operating reactors are invaluable.¹ One of the emerging techniques for such applications is NMR imaging (MRI).^{2–4} The MRI toolkit has been applied to study mass transport and chemical conversion in operating catalytic reactors.^{4–7} In particular, hydrogenation of unsaturated compounds has been addressed.^{8–11} For exothermic reactions such as catalytic hydrogenation, heat transport has a significant influence on the reactor operation. For instance, formation of stationary and traveling hot spots within the catalyst bed¹² can be disadvantageous and even disastrous. Therefore detection of temperature maps could be very useful for the optimization of reactor performance.

In principle, NMR thermometry is an existing technique. It is based on the temperature dependence of the sample characteristics that can be evaluated with NMR, such as the chemical shift, the relaxation time, the diffusivity, or the NMR signal intensity. Combined with the spatial resolution of the MRI modality, this approach can yield spatially resolved maps of sample temperature. In most such studies, including biomedical applications in vivo, the NMR thermometry approach based on the detection of the NMR signal of a liquid is employed.^{4,13,14} Unfortunately, this is not suitable for gas–liquid–solid multiphase systems such as trickle bed reactors because of the significant variation of the saturation of a porous catalyst with a liquid reactant during the reactor operation. This in itself leads to dramatic variations of all the temperature sensitive parameters listed above and thus renders them unreliable as temperature sensors. It appears, therefore, that the only feasible alternative is to use the NMR signal of the solid phase, for example, of the catalyst (support). This approach should be equally applicable to gas–liquid–solid and gas–solid processes at elevated temperatures. In our previous MRI studies of heterogeneous catalytic hydrogenation, we have used supported metal catalysts such as Pd/ γ -Al₂O₃.^{8–10} Both the intensity and the T_1 time of the ²⁷Al NMR signal of the support exhibit a pronounced temperature dependence, which was verified earlier using an external heating of the sample.¹⁵ In this work, the studies were for the first time extended to the 1D MRI thermometry of the catalyst bed in an operating catalytic reactor.

The experimental setup for the in situ MRI studies of heterogeneous catalytic hydrogenations has been described previously.^{8,9} In this study (Figure 1), the essential differences are the use of a gaseous reactant (propylene) and the detection of the ²⁷Al NMR signal of the solid phase (γ -Al₂O₃). During the experimental run which lasted continuously for over an hour, the flow of propylene was first increased in a stepwise manner, and then decreased during the second half of the experiment. Owing to the reaction exothermicity, this leads to the temperature variations within the catalyst bed as confirmed by the thermocouple measurements (Figure 2a, dotted line). The ²⁷Al NMR signal of the catalyst support, integrated

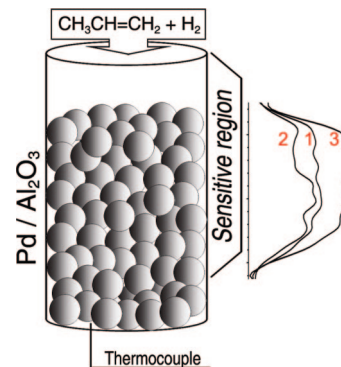


Figure 1. Schematic diagram of the reactor. Propylene and H₂ are supplied to the bed of 1 mm 1 wt % Pd/ γ -Al₂O₃ catalyst beads. A chromel-copel thermocouple is located in the lower part of the bed outside the sensitive region of the NMR probe. The three profiles labeled 1–3 reflect the ²⁷Al NMR signal intensity along the bed and correspond to the matching labels in Figures 2 and 3.

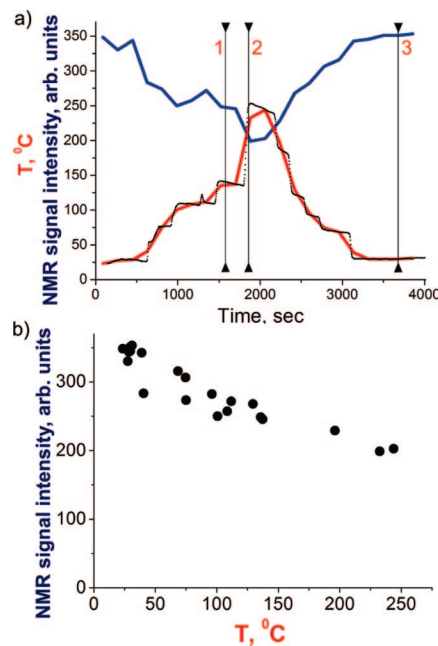


Figure 2. (a) Black dotted line shows the thermocouple temperature measurements performed every 3 s in the course of the hydrogenation experiment. These measurements were then averaged over the 3 min intervals (red line) corresponding to the intervals of the ²⁷Al NMR signal accumulation (blue line). Vertical lines labeled 1–3 indicate the time instants when the profiles shown in Figure 1 were acquired. (b) The data of Figure 2a presented as the dependence of the NMR signal intensity on the temperature measured with the thermocouple.

over the entire sensitive volume of the rf coil, is also shown in Figure 2a (blue line). The results demonstrate that signal intensity

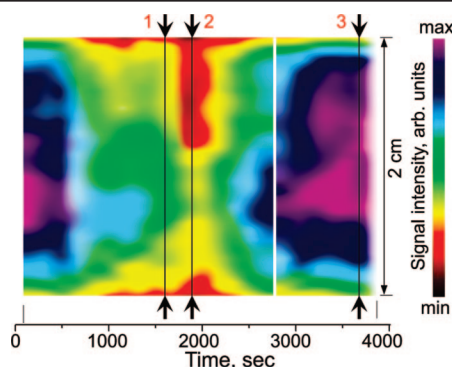


Figure 3. 1D profiles of the ^{27}Al NMR signal intensity along the vertical axis of the bed detected sequentially in the course of the experiment. The vertical axis corresponds to the spatial coordinate along the bed axis, the horizontal axis shows the time after the experiment was started, and the color scale reflects the NMR signal intensity (lower intensity corresponds to higher temperature). The 1D profiles labeled 1–3 are shown in Figure 1.

does change with temperature, as expected. This is further confirmed by Figure 2b, where the graph of Figure 2a is replotted as the dependence of the ^{27}Al NMR signal intensity on the temperature measured with the thermocouple. Figure 2b clearly demonstrates that variations of ^{27}Al signal intensity and of the catalyst temperature are indeed correlated. The primary reason for the NMR signal decrease with increasing temperature is the diminishing population difference between the nuclear spin sublevels and thus the decrease of the equilibrium magnetization of ^{27}Al nuclei. Additionally, the NMR signal detected can be sensitive to the variation of the nuclear spin relaxation times with temperature.¹⁵ For our approach to be valid, however, the signal intensity should be insensitive to the adsorption of gases at the gas–solid interface. In a dedicated control experiment, we have verified that under our experimental conditions the ^{27}Al NMR signal intensity of the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst measured at various temperatures remains unchanged when the catalyst is brought in contact with different gases (see Supporting Information). We note, however, that this may not be the case for other porous solids, especially those with higher specific surface area. Therefore, the validity of the approach will have to be checked if one uses different catalysts.

In the MRI experiment, the ^{27}Al NMR signal of Al_2O_3 was integrated in the radial direction of the bed but was spatially resolved along the bed axis. As a result, a set of 1D axial profiles with the spatial resolution of 0.83 mm detected sequentially ca. every 3 min during the hydrogenation experiment were acquired (Figure 3). The results demonstrate that as the temperature readings of the thermocouple go up (cf. Figure 2a), the signal intensity decreases along the entire part of the catalyst bed visualized in the experiment. At the same time, it can be seen that the changes in signal intensity depend on the axial coordinate and thus directly reflect the existence of temperature gradients in the axial direction. In particular, when the highest thermocouple readings are reached (ca. 250 °C), the results show that the temperature in the upper part of the catalyst bed is higher than in the rest of the bed. Significant local overheating of the upper part of the bed could be an indication that conversion of propylene into propane is almost complete in this part of the reactor. Later in the experiment, the temperature decreases as the reaction slows down, the chemical conversion in the upper part is no longer complete, and the axial temperature distribution becomes more uniform once again. The nonuniform variation of the signal intensity (temperature) is most apparent in Figure 1 where three individual profiles are shown

(vertical lines in Figure 2a and Figure 3 show when these profiles were detected during the experiment). These results provide the direct proof that the temperature distribution in the catalyst bed during the hydrogenation of gaseous propylene is not uniform. This is likely to be the reason for the apparent scatter of the data in Figure 2b. Indeed, the NMR signal presented in Figure 2 was averaged over the entire sensitive region of the rf probe, while the thermocouple measured the temperature at a single location in the lower part of the bed outside the sensitive region of the probe. In the presence of temperature gradients confirmed by the imaging experiment, this can lead to the pronounced differences between the NMR and the thermocouple measurements.

It would be useful to convert the measured ^{27}Al NMR signal intensity into the quantitative values of local temperature, but this is not possible at this time. Such conversion requires that an appropriate calibration is available. An insufficient sensitivity of the ^{27}Al MRI experiment currently prevents us from extending these studies to 2D and 3D temperature mapping. Both issues will be addressed in the ongoing research.

To summarize, we have implemented an MRI-based approach for the thermometry of an operating packed-bed catalytic reactor. This approach was employed for the spatially resolved NMR thermometry of the bed of $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst beads in the course of propylene hydrogenation reaction. This was achieved by detecting the spatially resolved axial 1D profiles of the ^{27}Al NMR signal intensity of Al_2O_3 in the course of the reaction. The experimental results demonstrate a clear correlation between the ^{27}Al NMR signal intensity and the catalyst temperature measured with a thermocouple (25–250 °C), and reveal the existence of pronounced temperature gradients along the catalyst bed.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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