Boosting resolution and sensitivity for operando studies of catalytic processes

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Introduction: In addition to the notorious sensitivity problem, magnetic resonance (MR) studies of heterogeneous objects suffer from a dramatic degradation of spectral resolution. This is particularly true about the studies of heterogeneous catalytic processes in operating reactors, with multiple gas-liquid-solid interfaces leading to a severe distortion of the applied magnetic field. An efficient solution to this problem required to fully utilize the power of the MR toolkit in the operando studies of catalytic reactors at an entirely new level is still lacking.

Methods: Our approach is based on the use of hollow spherical catalyst support particles. Their geometry and a reduced solid phase content largely improve magnetic field homogeneity, both in their interior and in the interparticle voids. The use of a granular bed of hollow alumina spheres ca. 2-3 mm in diameter with a 50 micron thick shell is shown to provide a significantly improved spectral resolution and image quality for liquids and gases within the bed.

Results and discussion: The linewidth of ^{1}H NMR signals of fluids in an NMR tube filled with hollow alumina spheres was reduced by more than 10-fold compared to fluids in ordinary granular beds [1] (Fig. 1a). Next, catalyst particles comprising rhodium nanoparticles supported on hollow alumina spheres were synthesized and tested in propylene hydrogenation, clearly demonstrating their advantages in terms of achievable resolution and sensitivity in operando MR studies of a catalytic process. MR images and spatially resolved NMR spectra clearly visualized the distribution of propylene (reactant) and propane (product) along the catalyst bed. Furthermore, the high spectral resolution achieved prevented the self-cancelation of absorption/emission NMR multiplets when parahydrogen instead of normal H_2 was used for NMR signal enhancement (Fig. 1b).

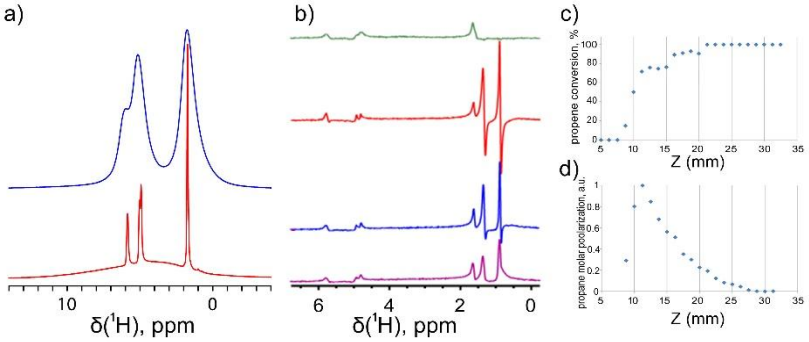

Fig. 1. (a) ^{1}H NMR spectra of propylene gas in a bed of ordinary (blue) and hollow alumina beads (red). (b) ^{1}H NMR spectra acquired during hydrogenation of propylene with parahydrogen with spatial resolution along the Rh/hollow-Al_2O_3 bed; the gas mixture is suppled from the top. (c) Propylene conversion and (d) propane molar polarization spatially resolved along the catalyst bed.

Conclusion: The use of hollow catalyst support particles opens the door for advanced operando studies of heterogeneous catalytic processes, providing sufficient spectroscopic and spatial resolution to monitor the distribution of reactants and products in the fluid phase of the reacting medium (Fig. 1c). Furthermore, the buildup and decay of parahydrogen-induced polarization within an operating catalyst layer was for the first time visualized with spatial resolution (Fig. 1d), providing the means for chemical engineering level optimization of a heterogeneous reactor to efficiently produce liquids and gases with the maximized molar hyperpolarization for a variety of applications.

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References: [1] Kononenko, Skovpin, Burueva, Rogozhnikov, Shefer, Salanov, Koptyug, Anal. Chem. (under review).