

Equipment for *in situ* flow MAS NMR studies of parahydrogen-induced polarization (PHIP) on solid catalysts

The technique utilized for *in situ* flow MAS NMR studies of the formation of parahydrogen-induced polarization (PHIP) on the surface and inside the pores of solid catalysts [1, 2] is based on a 7 mm *in situ* flow MAS NMR probe obtained by a Version 2 modification (see Section “flow probe 2”) of a commercial Bruker MAS NMR probe and an equipment schematically shown in **Fig. 1** (see Fig. 2 in Ref. [1], Fig. S2 in Supporting Information of Ref. [2], and Scheme 2 in Ref. [3]).

As shown in the scheme in **Fig. 1, left-hand side**, hydrogen gas flows from a bottle through a conversion reactor, filled with FeO(OH) catalyst (SIGMA-ALDRICH) and cooled in liquid nitrogen ($T = 77\text{ K}$), or through a by-pass. A filter behind the conversion reactor protects the valves and flow indicator against powder particles of the FeO(OH) catalyst. The FeO(OH) catalyst converts the common hydrogen (para-to-ortho ratio of 25% to 75%) into para-enriched hydrogen (para-to-ortho ratio of 50% to 50%). The hydrogen flow rate is adjusted via a needle valve and a flow indicator (rotameter). Before reaching the rotameter, the hydrogen gas is mixed with a reactant gas, e.g. ethene, propene etc., for studying the PHIP effect.

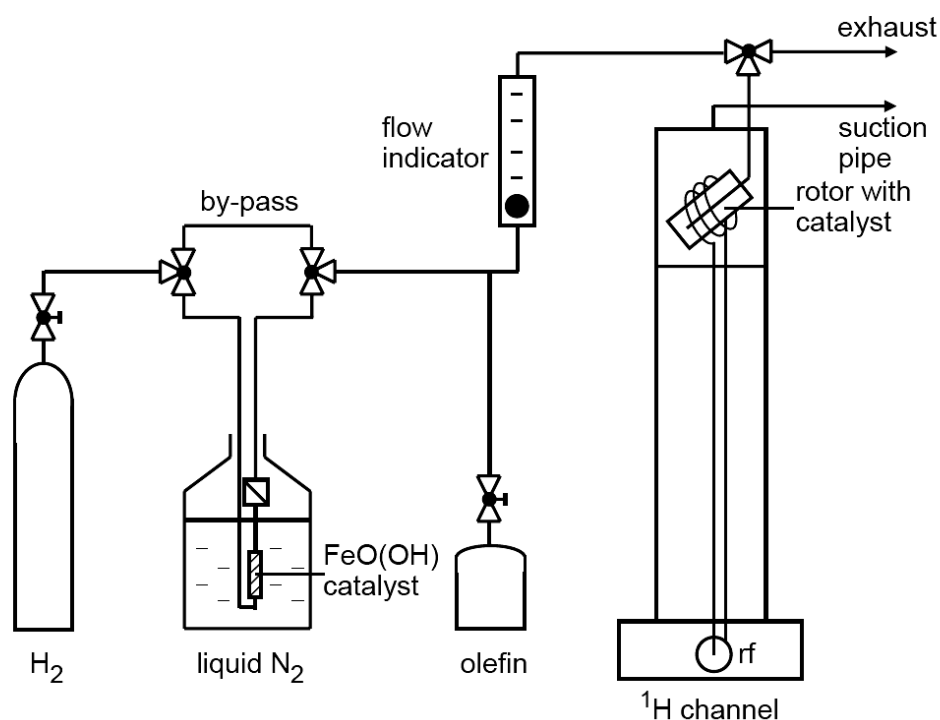


Fig. 1

The flow rate of this reactant is adjusted by a needle valve and determined by the rotameter via the flow rate increase. Finally, the reactant mixture (hydrogen/olefin) flows via a three-way cock into the *in situ* flow MAS NMR probe, during the PHIP experiment, or to an exhaust line (**Fig. 1, right-hand side**). For omitting hydrogen gas inside the magnet and in the laboratory atmosphere, the exhaust line and the exhaust of the *in situ* flow MAS NMR probe are connected with the suction pipe of the laboratory room.

Fig. 2 shows the self-made PHIP equipment with conversion reactor and particle filter, outside (left) and inside (right) of the liquid nitrogen bottle. The conversion reactor containing the FeO(OH) catalyst (**Fig. 3**) is made by a copper tube (1/4 inch), bent to a coil, and connected via a particle filter with the 1/8 inch stainless steel tubes of the PHIP equipment (left-hand side).



Fig. 2



Fig. 3

The hydrogen bottle is connected with the PHIP equipment at the **left-hand side in Fig. 2**, while the olefin bottle is connected at top of the equipment. Near these connectors, Swagelok SS-SS2-0 (0000439202) valves for the rough and fine adjustment of the gas flows are installed (**Figs. 4 and 5, top**). Three-way cocks Swagelok XJ2 XHD are used for switching between the by-pass and the conversion reactor in **Fig. 1**, left. The gas outlet is arranged in front of the image in **Fig. 5**.

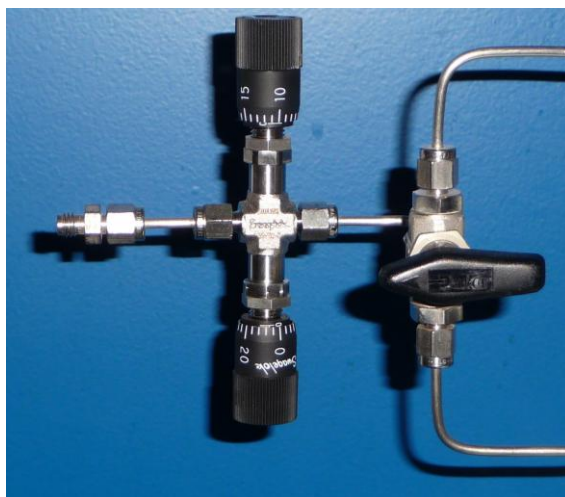


Fig. 4



Fig. 5

The correct function of the PHIP equipment is tested by investigating the ^1H NMR signal intensities of the hydrogen gas inside an empty MAS NMR rotor for flowing through the by-pass (i) and through the conversion reactor (ii) in **Fig. 1**. Since exclusively ortho-hydrogen atoms cause a ^1H NMR signal, the intensity of this signal should decrease from 100% to 67% after switching from (i) to (ii), i.e. from 75% to 50% ortho-hydrogen. Parahydrogen molecules cause ^1H NMR detectable polarization, if these molecules are pairwise incorporated into olefin molecules (ethene, propene etc.) on a solid hydrogenation catalyst inside the *in situ* flow MAS NMR probe (see, e.g., Refs. [1] and [2]) or on homogeneous hydrogenation catalysts of liquid reaction mixtures inside a sample tube (see e.g. Ref. [3]).

For initial approaches [1], PHIP experiments with different catalyst quantities inside the *in situ* MAS NMR rotor were tested (**Fig. 6** and Fig. 2 in Ref. [1]). For the hydrogenation of propene, rhodium-modified (0.4 wt.-%) zeolite Na-Y (0.4[Rh]Na-Y) was utilized. In these experiments, a 7 mm MAS NMR rotors was filled with 200 mg (**Fig. 6, left**) or 35 mg (**Fig. 6, right**) of this hydrogenation catalyst. In the latter case, the MAS NMR rotor contains a significantly larger empty gas volume in comparison with the former case.

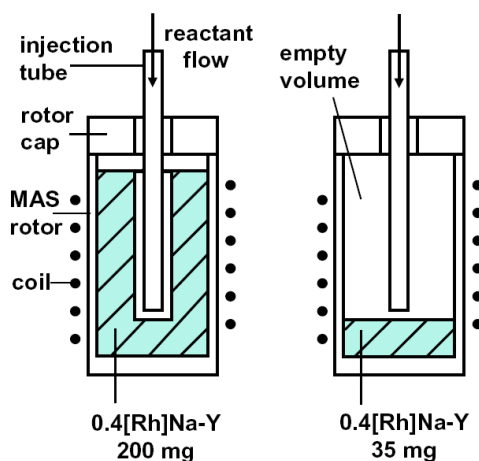


Fig. 6

In **Fig. 7**, the chemical shifts of the expected ^1H NMR signals of the reactant propene and the reaction product propane are summarized. The red-marked H^a and H^b atoms

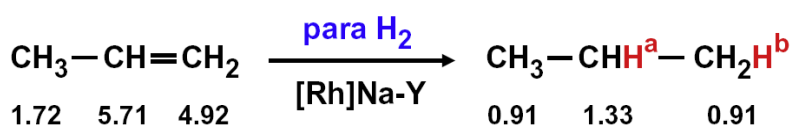


Fig. 7

are hyperpolarized species formed by a pairwise incorporation of para-hydrogen into propene molecules. These species cause typical anti-phase signals.

The ^1H MAS NMR spectra in **Figs. 8 and 9** clearly indicate that hydrogenation of propene on 0.4[Rh]Na-Y with para-enriched hydrogen leads to the formation of PHIP, as indicated by the typical anti-phase H^{a} and H^{b} signals. In the case of filling the MAS NMR rotors with the hydrogenation catalyst according to **Fig. 6, right**, the large empty gas volume has the advantage of a better detection of the hyperpolarized reaction products.

See Ref. [2] for further *in situ* MAS NMR investigations performed by utilizing the self-made PHIP equipment presented in this section and an *in situ* flow MAS NMR probe according to that described in Section “flow probe 2”.

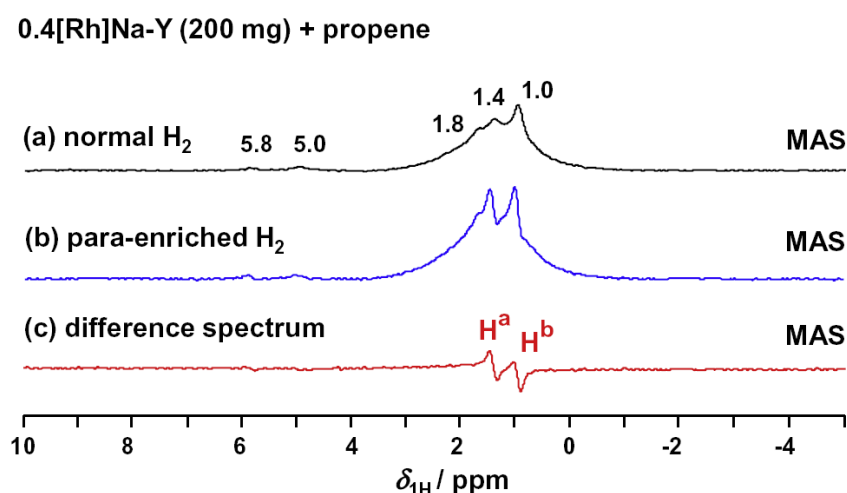


Fig. 8

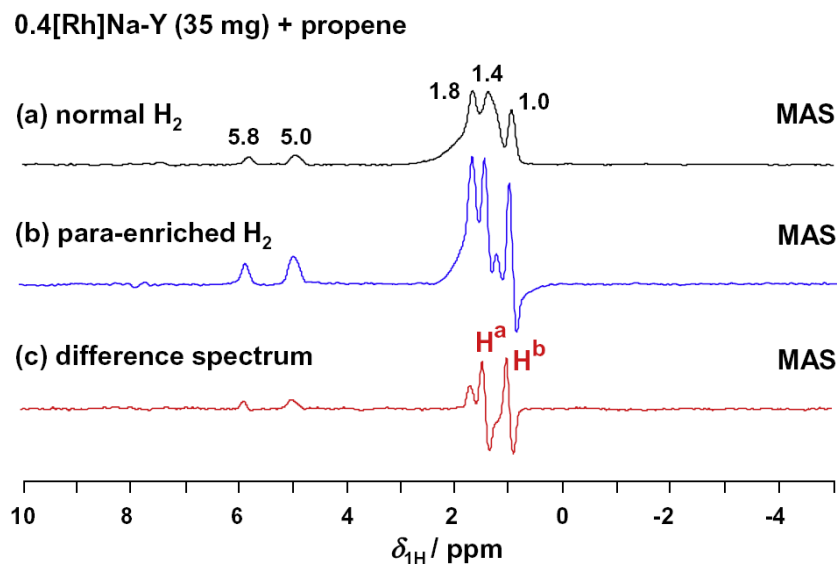


Fig. 9

References:

- [1] H. Henning, M. Dyballa, M. Scheibe, E. Klemm, M. Hunger, *In situ CF MAS NMR study of the pairwise incorporation of parahydrogen into olefins on rhodium-containing zeolites Y*, Chem. Phys. Lett. 555 (2013) 258-262, DOI: 10.1016/j.cplett.2012.10.068.
- [2] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, *In situ MAS NMR investigation of parahydrogen induced hyperpolarization inside meso- and micropores of Ir-, Pt-, Rh-, and Pd-containing solid catalysts*, J. Phys. Chem. C 121 (2017) 9953-9962, DOI: 10.1021/acs.jpcc.7b01899.
- [3] L.-S. Bouchard, K.V. Kovtunov, S.R. Burt, M. Sabieh Anwar, I.V. Koptug, R.Z. Sagdeev, A. Pines, *Para-Hydrogen-Enhanced Hyperpolarized gas-phase magnetic resonance imaging*, Angew. Chem. Int. Ed. 46 (2007) 4064-4068, DOI: 10.1002/anie.200700830.