Flow probe obtained by reversible modification of a Bruker MAS NMR probe

Two different modifications of commercial Bruker MAS NMR probes for obtaining *in situ* flow MAS NMR probes were performed (“flow probe 1” and “flow probe 2”). Version 1 is a reversible modification of a commercial Bruker MAS NMR probe so that *in situ* flow MAS NMR is performed with a probe, which can be back-converted into a standard MAS NMR probe. In contrast, Version 2 requires an irreversible modification of a commercial Bruker MAS NMR probe. The following description focuses on a Version 1 modification.

Fig. 1 shows a scheme of a MAS NMR stator modified according to Version 1 (see also Fig. 1 in Refs. [1] and [2]). The upper part of the sample lift is removed and a support for fixing an injection tube is added. This injection tube is inserted into the sample volume of a spinning MAS NMR rotor via a hole in the rotor cap. For excluding mechanical contact, the hole in the cap must be 0.2 to 0.5 mm in diameter larger than the outer diameter of the injection tube. Via the fixed glass tube acting as injection tube, purging gas (e.g. dry nitrogen), carrier gas loaded with reactants, or pure reactant gases are injected into the spinning MAS NMR rotor. The catalyst powder is pressed to a hollow cylinder so that an empty volume inside the rotor exists and no mechanical contact between the spinning catalyst and the fixed injection tube occurs. The reactants are injected at the bottom of the empty rotor volume, flow along the catalysts bed from bottom to top, and leave the rotor volume via an angular gap between the injections tube and the hole in the rotor cap.

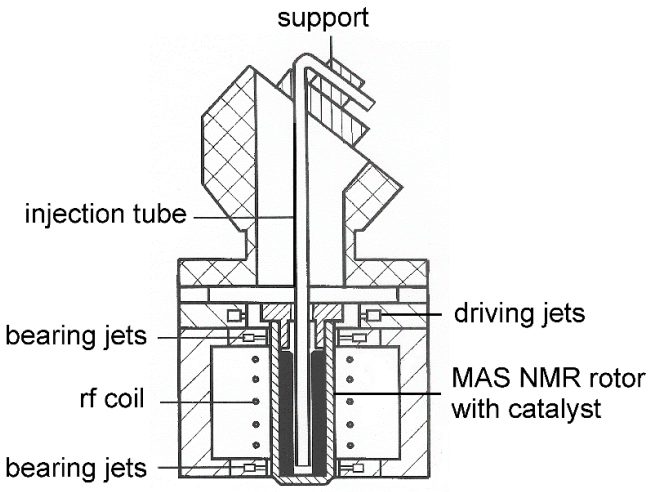

Fig. 1

Fig. 2 shows the injection tube support made by glass-fibre stabilized resin. Since the upper part of the sample lift of the commercial Bruker MAS NMR probe is fixed by two screws (**Fig. 3, left-hand side**), this way is also utilized to fix the injection tube support (**Fig. 3, right-hand side**). On top of this support, the injection tube is fixed by a plate and two screws. The self-made injection tube must be bent in such an angle that the lower part of this tube is centric in the spinning axis of the MAS NMR rotor, if this tube is inserted into the MAS rotor (**Fig. 2, right-hand side, bottom**).

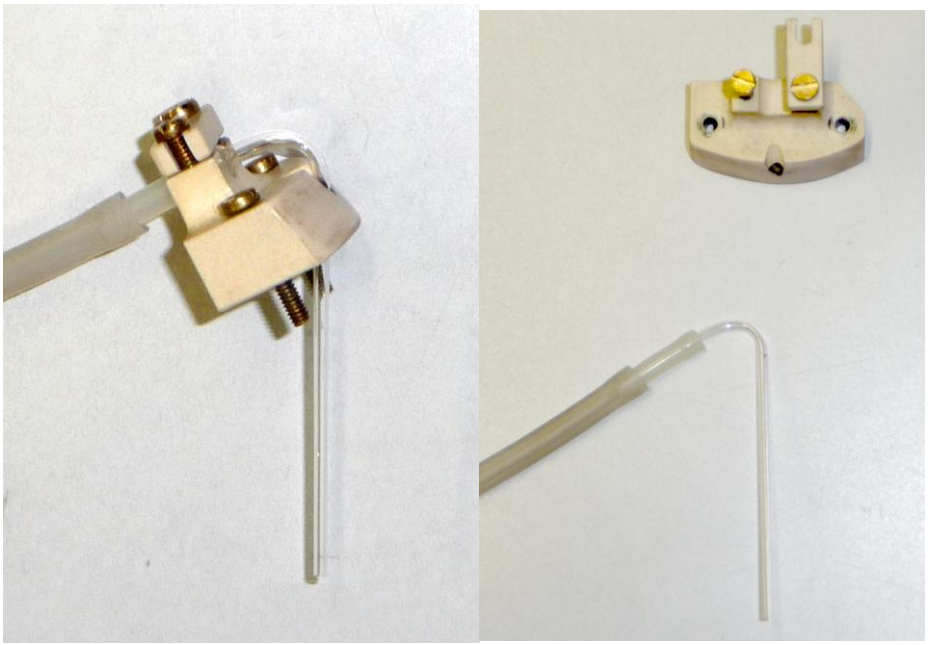

Fig. 2

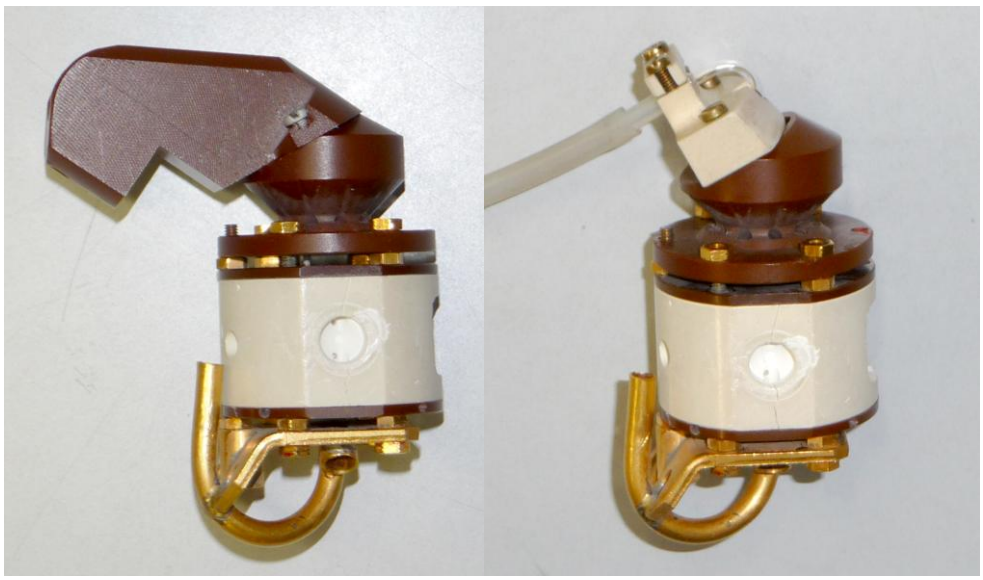

Fig. 3

For pressing the shape of the catalyst bed to a hollow cylinder, a tool as shown in **Fig. 4** is utilized. At first, the rotor is loosely filled with catalyst powder without to press it. Subsequently, this rotor is inserted into the acrylic glass part of the tool. At the bottom of this tool, the rotor can be fixed via a screw (**Fig. 4, right-hand side**). Then, the metal part of the tool **(Fig. 4, left-hand side)** is pressed into the catalyst powder inside the rotor. By slow removing this metal part, a hollow cylinder remains in the catalyst bed, which is required for the insertion of the injection tube.

Fig. 4

Commonly, the preparation of the activated catalyst inside the rotor using the tool in **Fig. 4** is performed in a mini glove box purged with dry nitrogen gas (see Section “mini glove box”). After pressing the catalyst bed, the rotor cap with a hole (**Fig. 4, bottom**) is added, Before, the hole in the cap was closed by a strip of TESA tape. Then, the rotor with the activated catalyst can be inserted into the stator of the modified *in situ* flow MAS NMR probe outside of the magnet and without air contact. Now, the support without the injection tube is fixed via the two screws. During purging of the upper part of the stator with dry nitrogen gas, the TESA tape is removed, and the spinning of the rotor is tested. This spinning is accompanied by a strong pressing of the cylindrical catalyst bed inside the rotor. If the spinning is suitable, the injection tube is inserted into the rotor volume. Subsequently, the injection tube is utilized for purging the activated catalyst inside the rotor with dry nitrogen gas for omitting air contact. Now, the glass housing shown in **Fig. 5** is put on top of the stator system and the metal housing of the MAS NMR probe is closed. Then, the *in situ* flow MAS NMR probe is inserted into the magnet.

Often, an exhaust tube is added on the glass housing in **Fig. 5** from top of the magnet. After successfully starting the spinning of the rotor and increasing the temperature to the desired value, the *in situ* MAS NMR experiment can be started by switching from purging gas to reactant gas.

Fig. 5

References:

[1] M. Hunger, T. Horvath, *A new MAS NMR probe for in situ investigations of hydrocarbon conversion on solid catalysts under continuous-flow conditions*, J. Chem. Soc., Chem. Commun. (1995) 1423-1424, DOI: 10.1039/c39950001423.

[2] M. Hunger, *In situ flow MAS NMR spectroscopy: State of the art and applications in heterogeneous catalysis*, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127, DOI: 10.1016/j.pnmrs.2007.08.001.