Flow probe obtained by irreversible 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 subsequently back-converted in a standard MAS NMR probe. In contrast, Version 2 is an irreversible modification of a commercial Bruker MAS NMR probe. The following description focuses on a Version 2 modification.

Fig. 1 (Fig. 1 in Ref. [1] and Fig. 2 in Ref. [2]) shows a scheme of a support for fixing an injection tube, which can be utilized for the injection of a reactant flow into the sample volume of a spinning MAS NMR rotor. For this purpose, the rotor cap has a hole for inserting the injection tube into the sample volume of the rotor without a mechanical contact with the rotor cap. The axis of the support is centrically arranged in relation to the spinning axis of the MAS NMR rotor. At the right-hand side, there are two gas line connectors, the first one for injecting the reactant gas and the second one for the injection of purging gas on top of the rotor cap or for the product gas outlet. In the subsequent Section "drawings", the detailed shapes of the support and the additional parts are shown. For the modification of a commercial Bruker MAS NMR probe according to these drawings, the upper part of the sample lift (**Fig. 2, left-**

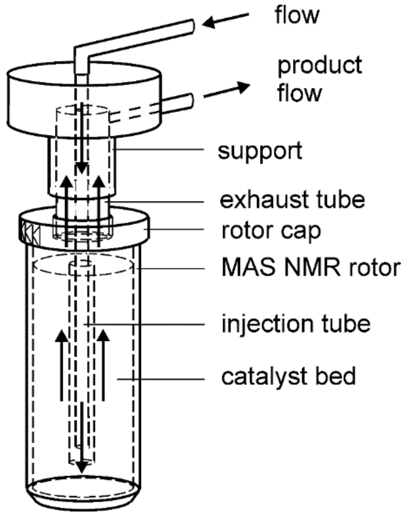

Fig. 1

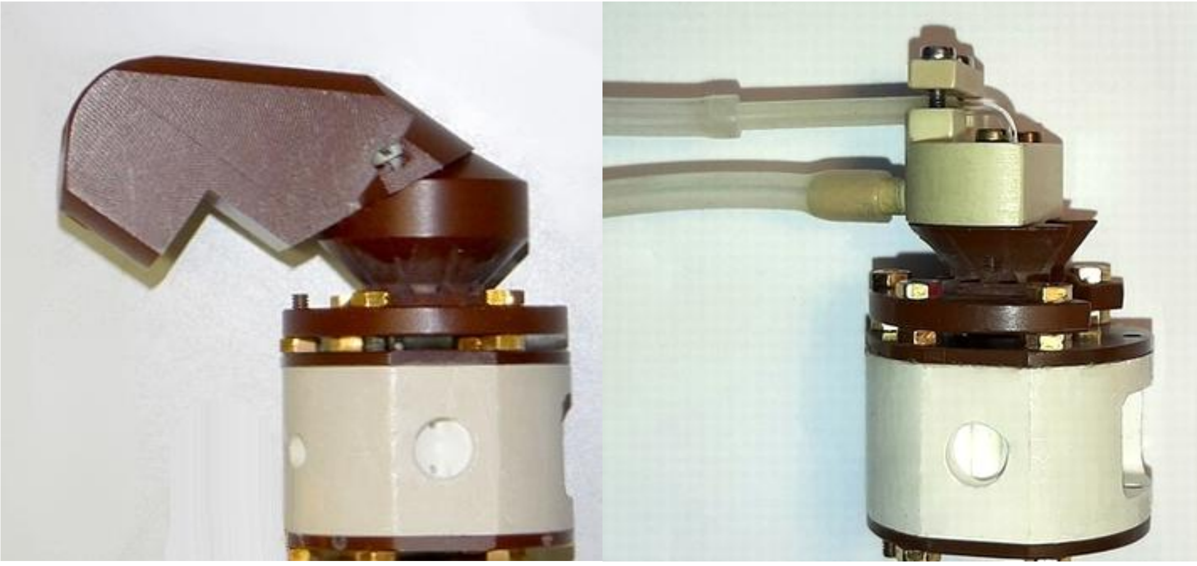

Fig. 2

hand side), which is fixed by two screws, must be removed. The lower part is modified in such a manner (see Part 5 in “drawings”) that the support (Part 1 in “drawings”) can be centrically arranged and fixed by two screws. The installed support is shown in **Fig. 2, right-hand side**. The injection tube (Part 6 in “drawings”) is inserted from top into the support and can be fixed by a plate (Part 2 in “drawings”) and two screws (**Fig. 3, left-hand side**). At the bottom of the support, a small cylinder can be inserted (Part 4 in “drawings”). The inner volume of this cylinder is connected with the lower gas connector (Part 3 in “drawings”). This connector is utilized for the injection of purging gas during the rotor preparation before starting the *in situ* experiments or as outlet of the product gas during the *in situ* MAS NMR experiment. **Fig. 3, right-hand side,** shows the modified lower part of the sample lift (Part 5 in “drawings”).

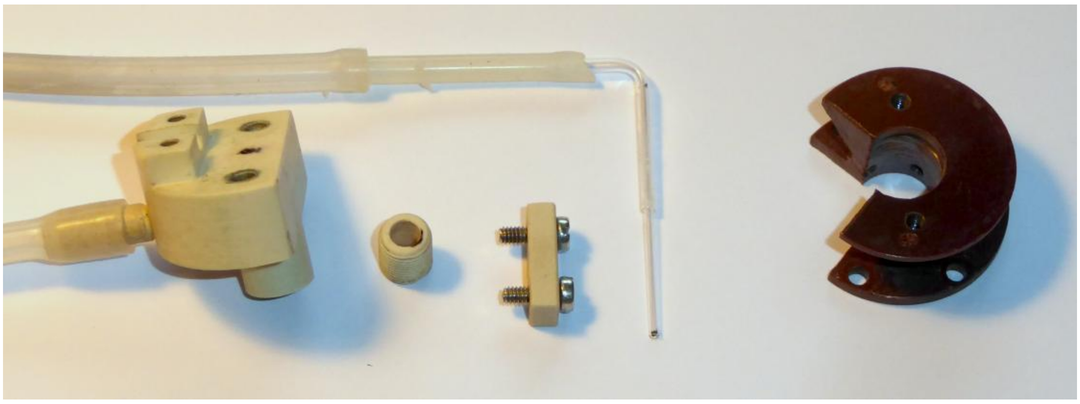

Fig. 3

The injection tube in **Figs. 3 and 4** is that used for a modified 4 mm MAS NMR probe (Part 6 in "drawings"). It consists of two parts. The lower part with an outer diameter of 1.00 mm (WILMAD) is inserted into the larger upper part and fixed by soluble alkali silicate (water glass). In the case of using a 4 mm MAS NMR rotor, the hole in the rotor cap has a diameter of 1.20 mm (**Fig. 4, middle**). A too large diameter of this hole in 4 mm rotor caps can damage the 4 mm cap during spinning.

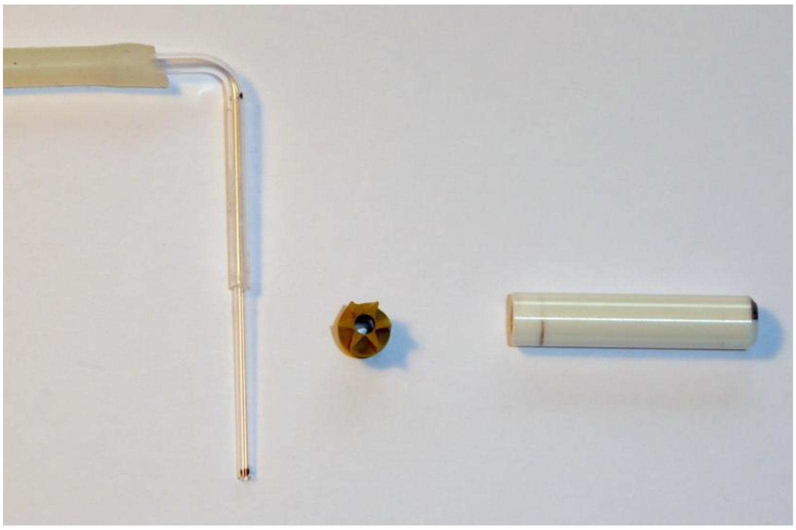

Fig. 4

In the case of using 7 mm MAS NMR rotors, the injection tube has an outer diameter of 1.8 mm. A second tube with an outer diameter of 3.0 mm, which is inserted at the bottom of Part 4, can be utilized as an exhaust for the reaction products. Both, the injection tube and the exhaust tube are inserted into the rotor via the hole in the 7 mm rotor cap with the diameter of 3.2 mm. By this way, the reaction products can leave the rotor at the top via the exhaust tube, which is connected with the sampling loop of an *on-line* gas chromatograph.

For the modification of the lower sample lift part (Part 5 in "drawings"), the tool shown in **Fig. 5** was utilized. It allows the fixing of Part 5 in a lathe.

For pressing the shape of the catalyst bed inside the MAS NMR rotor to a hollow cylinder, a tool as shown in **Fig. 6** is utilized. At first, the rotor is loosely filled with activated catalyst powder without to press it. Subsequently, the rotor is inserted into the acrylic glass part of the tool. At the bottom of this tool, the rotor can be fixed by a screw (**Fig. 6, right-hand side**). Then, the metal part of the tool is pressed into the catalyst powder inside the rotor. By slow removing this metal tool, a hollow cylinder remains in the catalyst bed, which is required for the insertion of the injection tube.

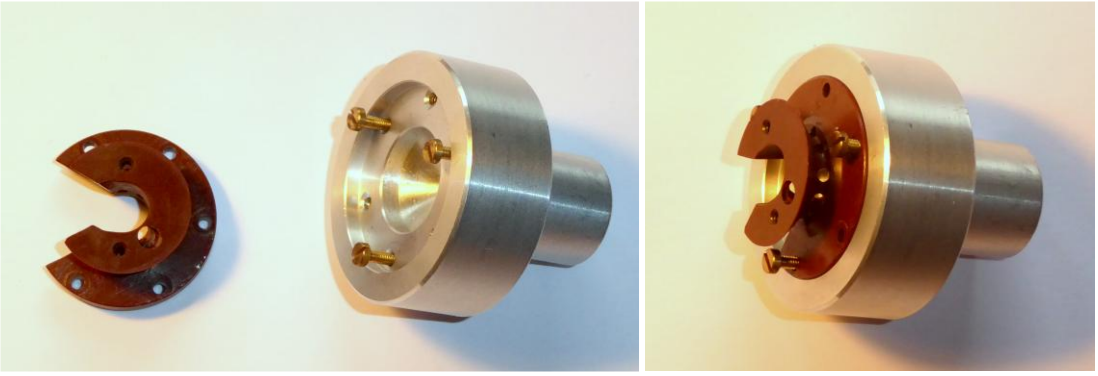

Fig. 5

Fig. 6

Commonly, the preparation of the activated catalyst inside the rotor using the tool in **Fig. 6** 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 containing a hole (**Fig. 6, bottom**) is pressed on top of the rotor. For excluding ambient air contact during the rotor transfer, the hole in the rotor cap is closed by a strip of TESA tape. Subsequently, the rotor with the activated catalyst is transferred into the stator of the modified *in situ* flow MAS NMR probe. For this purpose, the probe is outside of the magnet and the probe housing as well as the support (Part 1 in "drawings") are removed. Subsequently, the support without the injection tube is fixed via the two screws (**see Fig. 7**). Upon starting the purging gas flow (via connector Part 3 in "drawings"), the upper part of the stator and the rotor cap are covered with

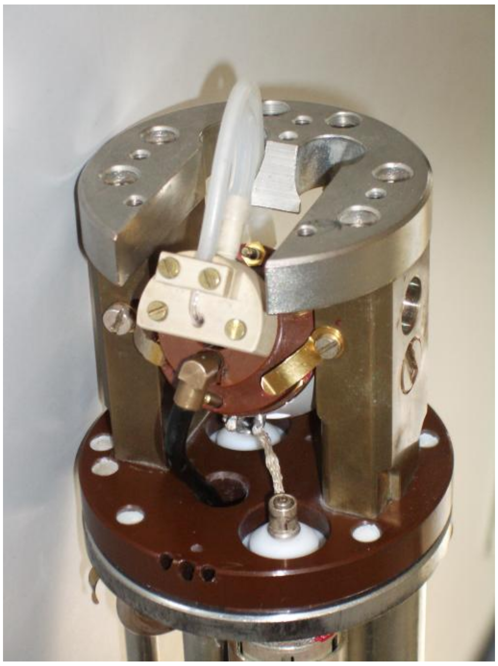

Fig. 7

dry nitrogen gas. Therefore, the TESA tape can be removed, without contamination of the activated catalyst by air. Now, the spinning of the rotor is tested. The spinning is accompanied by a strong pressing of the cylindrical catalyst bed inside the rotor. If the spinning is suitable, it is stopped again, the glass housing shown in **Fig. 8** is put on top of the stator system and the metal housing of the probe is closed. Then, the *in situ* flow MAS NMR probe is inserted into the magnet. In some cases, an exhaust tube is arranged on top of the glass housing in **Fig. 8** for removing reactant gases from the magnet. After the successful start of the rotor spinning inside the magnet with dry nitrogen gas, the purging gas at connector Part 3 can be stopped. Now, the

Fig. 8

in situ experiment can be started by switching the reactant gas flow to the injection tube (Part 6 in “drawings”). In the **Attachment**, a survey of the **“work flow”** containing the different steps of *in situ* flow MAS NMR experiments is given.

References:

[1] M. Hunger, M. Seiler, T. Horvath, *A technique for simultaneous in situ MAS NMR and on-line gas chromatographic studies of hydrocarbon conversions on solid catalysts under flow conditions*, Catal. Lett. 57 (1999) 199-204, DOI: 10.1023/A:1019064003201.

[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.

Attachment:

Work flow of *in situ* MAS NMR experiments

Step	Equipment	Procedure
1	vacuum line 1	dehydration and activation of the catalyst powder; subsequent, sealing in a glass tube until its use in an *in situ* experiment
2	mini glove box, purged with dry nitrogen gas	transfer of the activated catalyst from the glass tube into the MAS rotor under a dry nitrogen flow inside a glove box; shaping of the catalyst powder to a hollow cylinder using the tool shown in Fig. 6; sealing of the MAS rotor with a cap, which has a centric hole closed by a strip of TESA tape (length ca. 10 mm, width as required to tightly seal to hole in the rotor cap)
3	flow probe 2	the MAS rotor containing the activated catalyst and sealed with the TESA tape is inserted into the modified and open (the “support” in Fig. 3, left, or Part 1 in “drawings” is removed) MAS NMR stator
4	flow probe 2	the “support” is fixed at Part 5, i.e. on top of the modified the stator with two screws M2 (length ca. 14 mm) without inserting the injection tube Part 6
5	flow probe 2	the purging line connected via Part 3 at Part 1 is used to inject a flow of dry nitrogen gas (ca. 20 ml/min) at the top of the inserted MAS NMR rotor; now, the TESA tape is removed and no contamination of the activated catalyst in the rotor by humidity or other impurities can occur due to the nitrogen purging on top
6	flow probe 2	start spinning of the rotor using dry nitrogen gas for bearing and driving; by the spinning, the catalyst bed is further pressed to a hollow cylinder; stop spinning, but don’t stop purging flow on top of the MAS rotor
7	flow probe 2 equipment 1	start flow of dry nitrogen gas (ca. 5 ml/min) through the injection tube Part 6; insert the injection tube into Part 1; fix the silicon tube with the injection tube with Part 2 and two screws M2 (length ca. 8 mm) on top of Part 1
8	flow probe 2	test slowly spinning of the MAS rotor with the inserted injection tube until the spinning rate can be increased up to the required value; nitrogen purging via the purging line connected with Part 3 is continued; stop spinning

9	flow probe 2	close the probe head housing and insert the probe head into the magnet; start spinning again and continue to spin for tuning and test measurements; now, the nitrogen purging on top of the stator can be stopped
10	flow probe 2	tuning and start of the reference measurements of the activated catalyst
11	flow probe 2 equipment 1	adjust reactant flow, which goes at first to the exhaust line; if this flow is stable, switch from nitrogen flow through the injection tube to the reactant flow; start the *in situ* MAS NMR experiment