Sample tube system for *in situ* MAS NMR studies under batch conditions

Commercial glass inserts for MAS NMR rotors are useful for studying the conversion of reactants on solid catalysts under batch conditions. In this case, the reaction systems are sealed in small glass ampoules, which can be heated in an external oven without air contact or loss of reactants before their study via solid-state NMR. For this purpose, the glass insert is connected with a vacuum valve system, which allows the connection with a vacuum line as shown in the scheme of **Fig. 1, left-hand side** (Fig. 7 in Ref. [1], Fig. 9 in Ref. [2], Fig. 2.4 in Ref. [3]). After sealing the constriction of the glass insert containing the catalyst sample, the obtained glass ampoule is introduced into the MAS NMR rotor as schematically shown in **Fig. 1, right-hand side.**

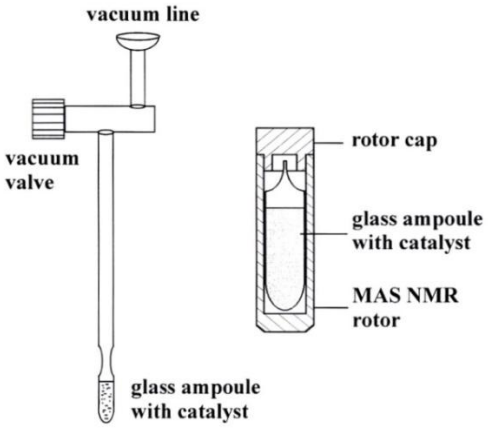

Fig. 1

Often utilized glass inserts are PYREX MAS inserts offered by WILMAD and suitable for Bruker 4 mm or 7 mm rotors (**Fig. 2, left**). Another way is the use of self-made inserts utilizing a glass-pulling-device, such as shown in the Attachment. The glass inserts are connected with common glass tubes, such as DURAN glass tubes (**Fig. 2, right**), which are also used for the sample tubes described in Section “sample tube system 1”.

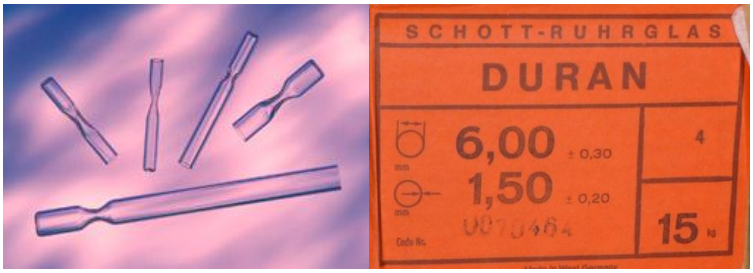

Fig. 2

In **Fig. 3, top**, the sample tube system including the joint PYREX MAS insert, the vacuum valve, and the vacuum connector described in Section “sample tube system 1” is shown. **Fig. 3, bottom**, is an enlargement of the PYREX-DURAN connection.

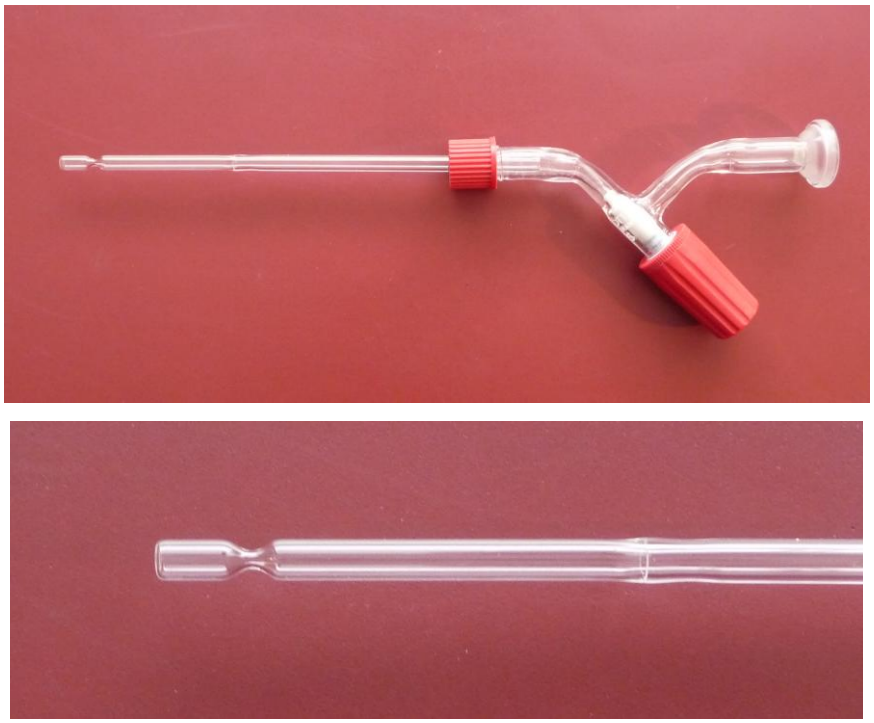

Fig. 3

The sample preparation with the sample tube system in **Fig. 3, top**, is performed as described for the common sample tube system in Section “sample tube system 1”. After the filling of the glass insert, the user must have attention that no powder material remains in the insert constriction. If there is powder material during the sealing of the insert constriction, the obtained glass ampoule may be not gas-tight. If possible, the sealing should be performed using a double-flame gas burner as that shown in **Fig. 4**.

Fig. 4

Independent on the type of the gas burner, the sample material inside the ampoule of the insert must be protected against heating during the sealing. Therefore, sealing in two steps is suggested. The first step is the sealing of the DURAN glass tube, far away from the glass insert with the sample material (**Fig. 5a**). By this sealing, the vacuum valve is removed and the remaining short sample glass tube is easier to handle. The second sealing step is performed with the glass insert, containing the catalyst sample, in a strongly cooled state (**Fig. 5b**). For this purpose, this part of the insert is introduced into a clamp jaw with suitable inner diameter, which is cooled down in a dewar with liquid nitrogen. This procedure has the advantage of protecting the sample material against heating.

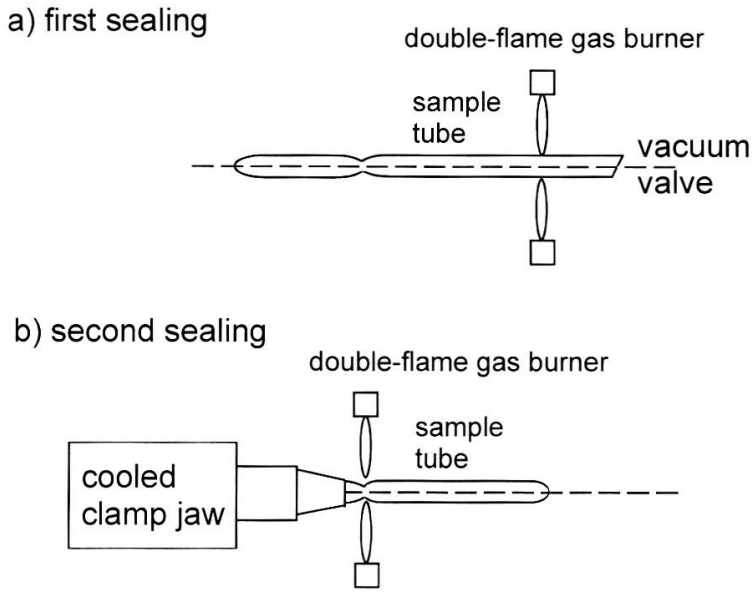

Fig. 5

A suitable clamp jaw (**Fig. 6, top**) can be that of the lathe shown in **Fig. A1** of the **Attachment**. The clamp jaw is connected with a large metal tube, which has a high heat capacity and helps to handle the clamp jaw during the sealing. Both together fit well in a dewar, which is filled with liquid nitrogen (**Fig. 6, bottom**). After the glass insert with the sample material is put into the clamp jaw and cooled down in liquid nitrogen, the insert is sealed at the insert constriction as shown in **Fig. 5b**. Since the glass walls of the inserts are very thin, the constriction of the insert is moved through the flames of the gas burner for short times only. After successful sealing, a glass ampoule like that shown in **Fig. 7** is obtained. This ampoule fits well into a

commercial MAS rotor and is able to spin under MAS conditions, often with a slightly increased bearing pressure.

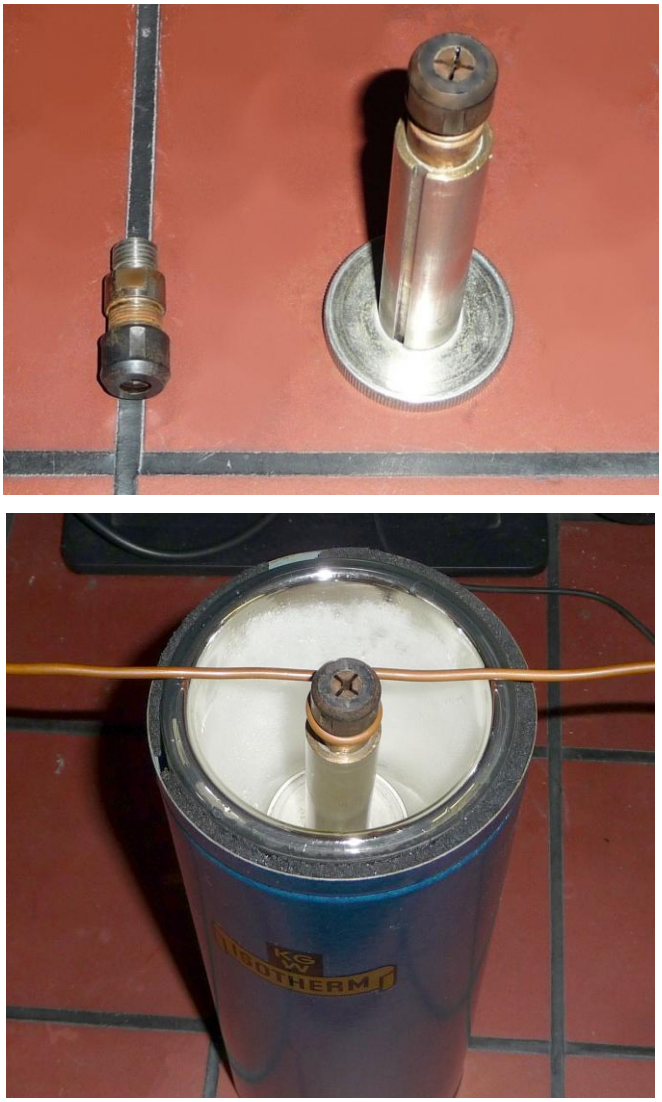

Fig. 6

Fig. 7

Attachment:

Fig. A1 shows a self-made lathe utilized as glass-pulling-device for the preparation of glass inserts for applications as sample ampoules in MAS rotors. The electric engine

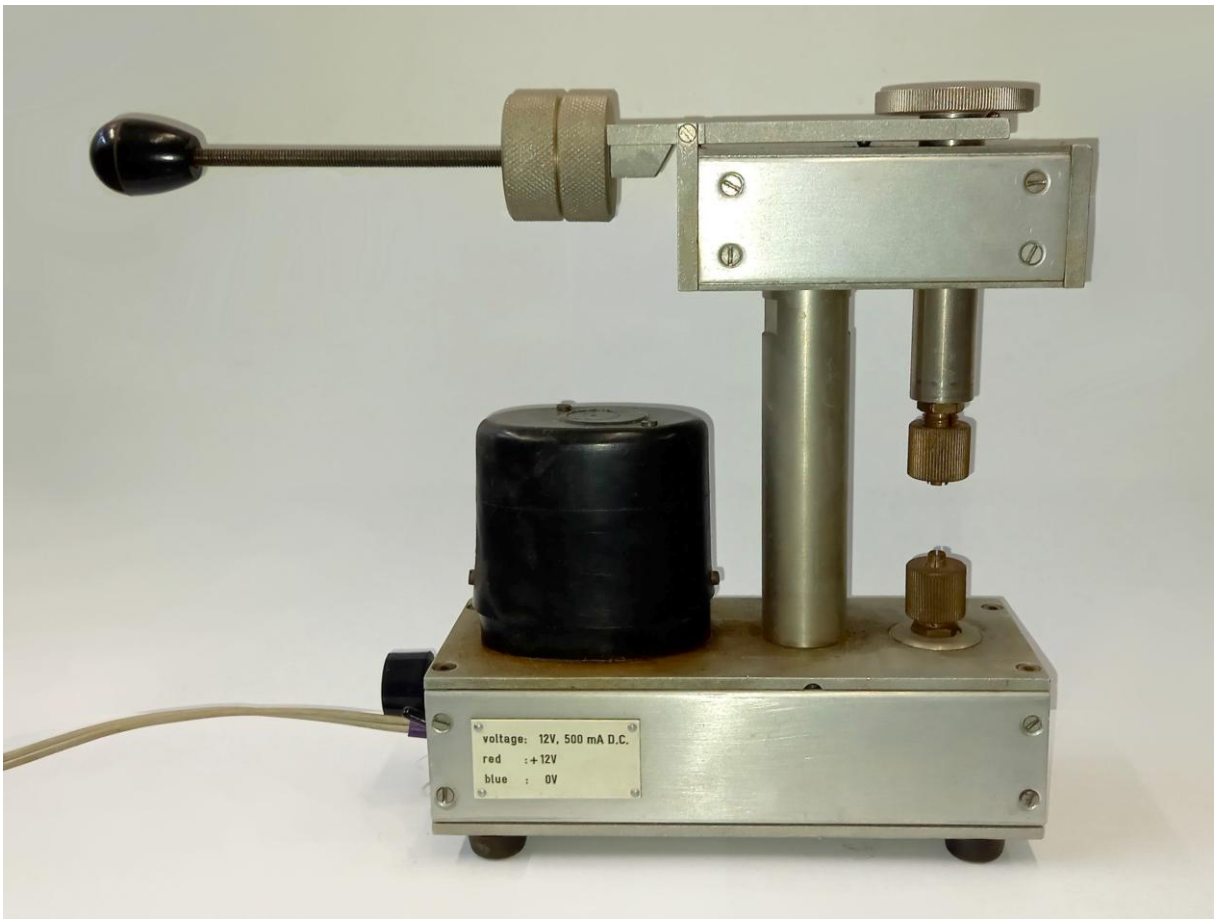

Fig. A1

In the black housing on the left-hand side is mechanically connected via a gear box with the two clamp jaws on the right-hand side, bottom and middle. While slowly spin the glass tube (e.g. common WILMAD tubes), fixed in the two clamp jaws, the double-flame gas burner shown in **Fig. 4** is utilized for heating the slowly rotating (0.5 to 1 s^{-1}) glass tube. If the glass tube starts to melt, the distance between the two clamp jaws is slowly increased by moving down the black handle on the left-hand side in **Fig. A1**. By this way, the hot glass tube is totally closed, such as necessary for preparing the bottom of a glass insert. In a second step, the slightly melted glass tube is narrowed only, such as necessary for preparing the constriction at the top of a glass insert.

Reference:

[1] M. Hunger, W. Wang, *Characterization of Solid Catalysts in the Functioning State by Nuclear Magnetic Resonance Spectroscopy*, Adv. Catal. 50 (2006) 149-225, DOI: 10.1016/S0360-0564(06)50004-5.

[2] M. Hunger, J. Weitkamp, *In situ Magnetic Resonance Techniques: Nuclear Magnetic Resonance*, in: B.M. Weckhuysen (ed.), *In situ Spectroscopy of Catalysts*, American Scientific Publishers, Stevenson Ranch, California, 2004, ISBN: 978-1-4020-9678-5, p. 177-218.

[3] M. Hunger, *Solid-State NMR Spectroscopy*, in: A.W. Chester, E.G. Derouanne (eds.), *Zeolite Characterization and Catalysis - a Tutorial*, Chapter 2, Springer-Verlag, Berlin, 2009, ISBN: 978-1-4020-9678-5, p. 65-106.