Equipment for combined *in situ* flow solid-state NMR and catalytic studies with on-line gas chromatography

The *in situ* flow MAS NMR combined with on-line GC technique is based on the coupling of a 7 mm *in situ* flow MAS NMR probe, obtained by modification of a commercial Bruker MAS NMR probe (see Section “flow probe 2”), and a catalytic equipment with on-line gas chromatographic (GC) analysis of reaction products. The simplest version of this technique is schematically shown in **Fig. 1** (see also Fig. 2 in Ref. [1] and Fig. 6 in Ref. [2]).

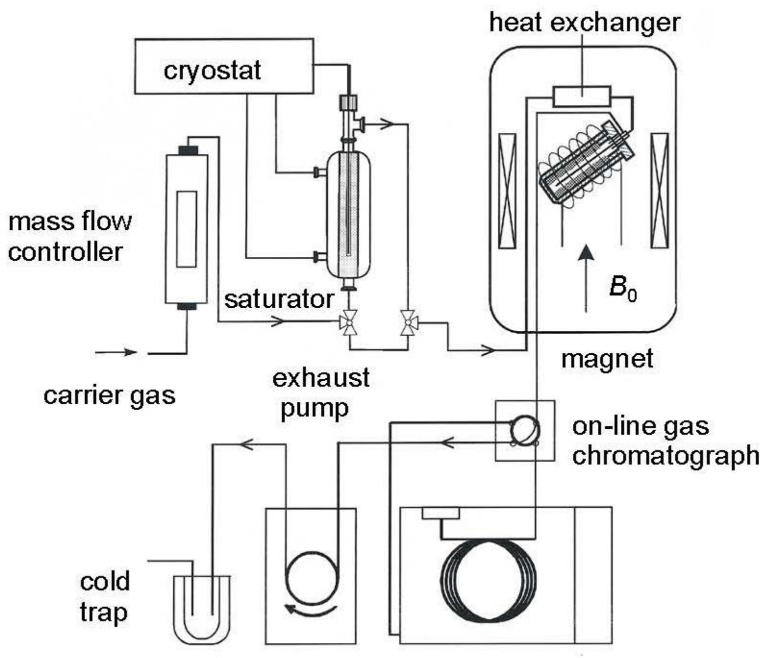

Fig. 1

An important part of the equipment in **Fig. 1** is the reactant supply system schematically shown in **Fig. 2**. It was developed for a flexible experiment design, such as for using pure reactant gas (input 1) and up to three kinds of liquid reactants loaded on carrier gas (input 2/N_2) requiring specific saturators. Therefore, it contains three mass-flow controllers and a rotameter for the adjustment of high gas flows, e.g. for purging the tubes or the *in situ* MAS NMR rotor with pure carrier gas. The above-mentioned reactant flows are used for catalysis inside the *in situ* flow MAS NMR probe (Out1/NMR) or in a standard fixed-bed reactor (Out1/Reactor), e.g. for comparing reactions in these two reactor systems.

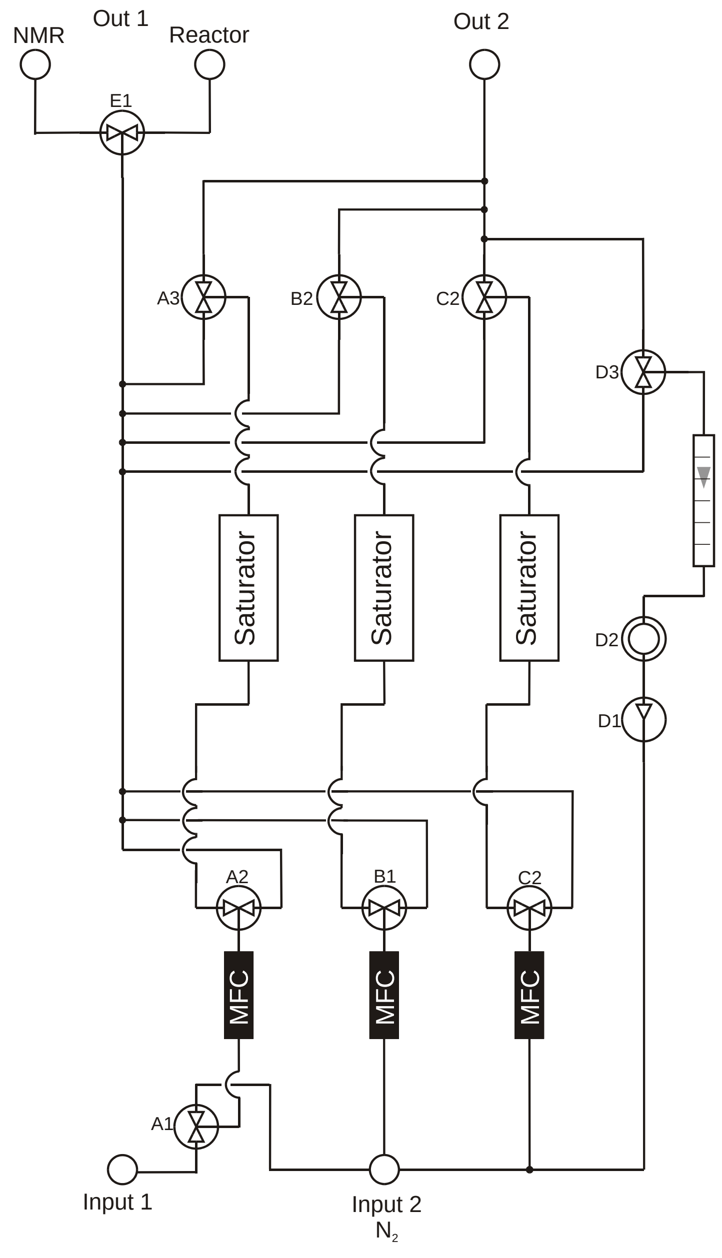

Fig. 2

The reactant supply system is the black panel in the middle of **Fig. 3**. It shows three fixings for saturators, the right position is used to fix a saturator in this image. The mass-flow controllers (BRONKHORST) are installed at the backside of the panel, while their displays are in the front (**Fig. 4, right-hand side, top**). At the left-hand side in **Fig. 3**, a standard fixed-bed reactor connected with Out1/Reactor inside a laboratory oven is arranged. The black box with the WEST 4400 temperature controller is utilized for controlling the oven containing the fixed-bed reactor. A flexible tube goes from Out1/NMR via a hole in the laboratory room wall behind the equipment to the reactant flow inlet of the *in situ* flow MAS NMR probe in the neighbouring spectrometer room.

Fig. 3

Fig. 4

Some of the saturators were specifically constructed for the loading of expensive isotopically enriched reactants on the carrier gas (**Fig. 5**). With these saturators, it is possible to obtain a well-saturated carrier gas by injecting small amounts of these reactants into the saturator.

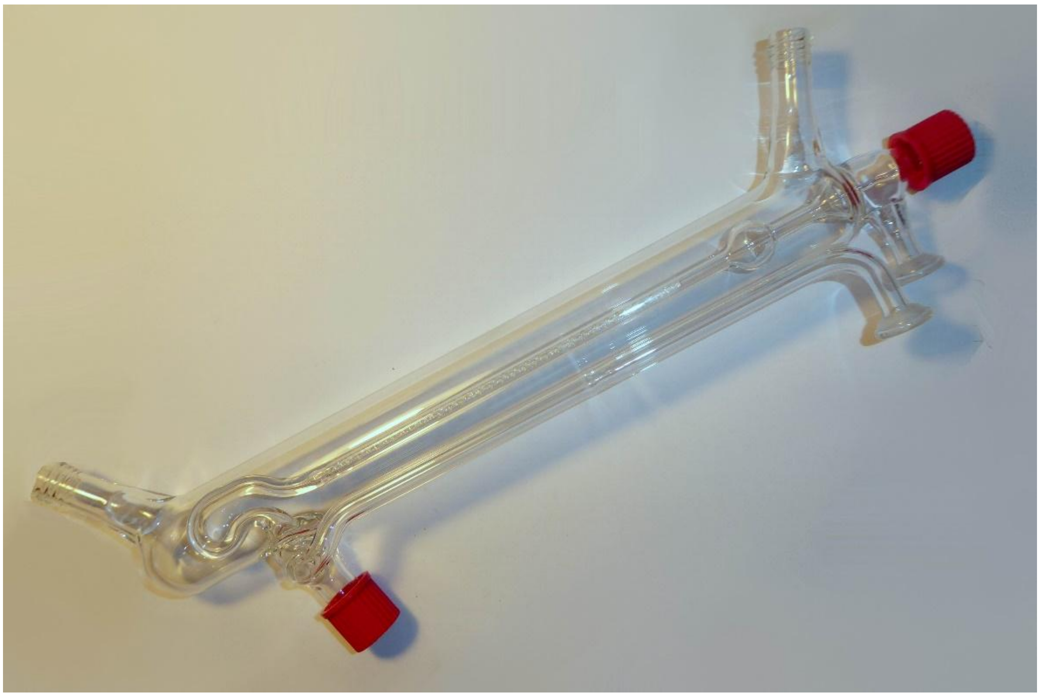

Fig. 5

For this purpose, the reactants are injected via a septum into the lower part of the saturator (**Fig. 6, top**). Exclusively the small glass balls inside the inner tube of the saturator, which is purged by the carrier gas, are covered by the injected reactants. A glass stick on top of the saturator hinders the glass balls to leave the inner saturator tube in the case of high carrier gas flows (**Fig. 6, bottom**). The outer volume of the saturator is used for heating or cooling the saturator via a temperature controlled liquid. In most of the experiments, the saturators are applied at a temperature, which is ca. 10 K lower in comparison with the laboratory room temperature. In this case, no condensation of reactants loaded on the carrier gas occurs inside the tubes between the reactant supply system and the *in situ* flow MAS NMR probe. A cryostat at the left-hand side of the gas chromatograph is utilized for the cooling the liquid used for the temperature control of the saturators (**Fig. 4, bottom**). After the catalytic conversion of the reactants inside the *in situ* MAS NMR probe, the reaction products leave the modified MAS NMR stator via the lower gas connector in Fig. 1 of Section “flow probe 2”. These reaction products are sucked off from the *in situ* flow MAS NMR rotor using a peristaltic pump (**Fig. 3, lower middle position**).

Fig. 6

The peristaltic pump of type MCP Memory 6.05 by ISMATEC (Fig. 7) is arranged behind the sampling loop on top of the on-line gas chromatograph (see **Fig. 1**). The flexible tubes between the product outlet of the *in situ* flow MAS NMR probe and the sampling loop and between the sampling loop and the inlet of the chromatograph as well as the sampling loop are heated using heating wires delivered by the HORST company and RS temperature controllers (**Fig. 4, top, middle**).

Fig. 7

The UV/Vis spectrometer of Avantes located between the black temperature controller box and the gas supply system in **Fig. 3** can be used for *in situ* UV/Vis studies of reactants inside the fixed-bed reactor in the external oven at the left-hand side. For this purpose, a high-temperature glass fibre UV/Vis probe of type HPSUV1000A by Oxford Scientific Instruments, shown in Fig. 5 of the Section “equipment 2“, accessible via link “*In Situ* Solid-State NMR Techniques”, is applied. This UV/Vis probe is inserted into the fixed-bed reactor from top via a septum containing holes with the size of the outer diameter of the glass fibres.

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.