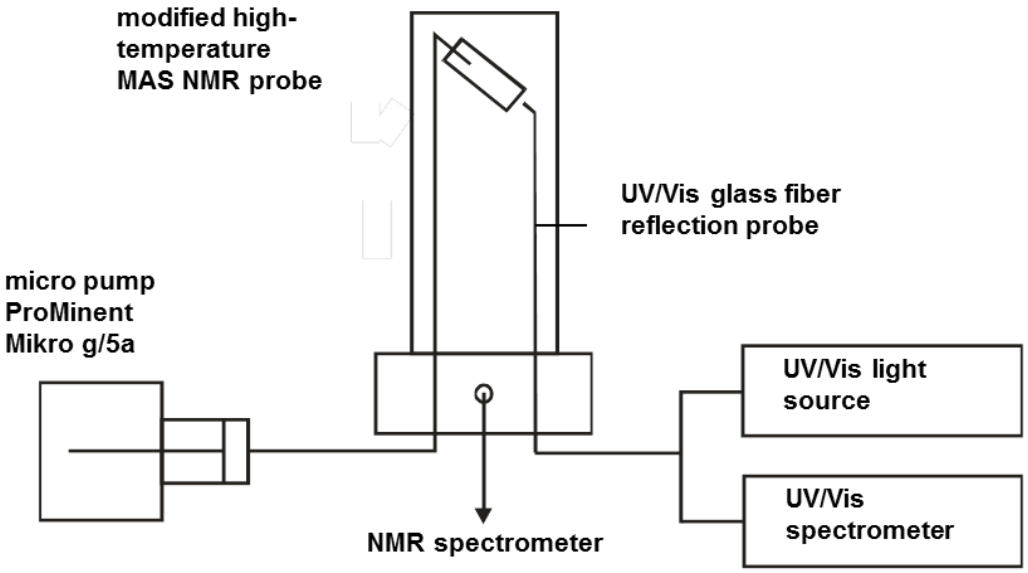
Equipment for *in situ* pulsed-flow solid-state NMR spectroscopy

The equipment utilized for *in situ* pulsed-flow NMR experiments allows the rapid injection of liquid reactants into a spinning MAS rotor at a well-defined start time (Fig. 7d in Ref. [1]). The equipment in **Scheme 1** is based on a 7 mm *in situ* flow MAS NMR probe, obtained by modification of a commercial BL-type Bruker MAS NMR probe (see Section “flow probe 2”) or of a high-temperature 7 mm STD MAS NB NMR probe of type DSI-740 produced by DOTY Scientific Instruments, USA (see Section “flow probe 4”, Ref. [2] and Fig. 4 in Ref. [3]).



Scheme. 1

For injecting well-defined amounts of liquid reactants into an MAS NMR rotor containing the activated catalyst [4], a pump of the type Mikro g/5 by ProMinent, Germany, allowing single pulses with volumes of 2 to 50 µl, is utilized (**Fig. 1, left-hand side**). If required, the pulses of this pump can be started by computer. For H/D exchange experiments, the suction line of the pump is directly inserted into the vessel containing the deuterated reactant (**Fig. 1, right-hand side**). Upon injection of small volumes of liquid reactants into a spinning 7 mm rotor containing the activated catalyst, the spinning speed goes shortly down for ca. 500 Hz and is stabilized again after 2 to 4 s.

Fig. 1

If required, *in situ* pulsed-flow solid-state NMR spectroscopy is combined with *in situ* UV/Vis spectroscopy (right-hand side of **Scheme 1**) described in Section “flow probe 3”. In this case, two complementary spectroscopic methods are simultaneously utilized under *in situ* conditions.

References:

[1] 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.

[2] Y. Jiang, J. Huang, V.R. Reddy Marthala, Y.S. Ooi, J. Weitkamp, M. Hunger, *In situ MAS NMR-UV/Vis investigation of H-SAPO-34 catalysts partially coked in the methanol-to-olefin conversion under continuous-flow conditions and of their regeneration*, Microporous Mesoporous Mater. 105 (2007) 132-139, DOI: 10.1016/j.micromeso.2007.05.028.

[3] M. Hunger, *Moderne Methoden der In-situ-Festkörper-NMR-Spektroskopie in der heterogenen Katalyse*, Chemie Ingenieur Technik 79 (2007) 781-793, DOI: 10.1002/cite.200700008.

[4] J. Huang, Y. Jiang, V.R. Reddy Marthala, Y.S. Ooi, M. Hunger, *Regioselective H/D exchange at the side-chain of ethylbenzene on dealuminated zeolite Y studied by in situ pulsed-flow ^{1}H MAS NMR-UV/Vis spectroscopy*, ChemPhysChem 9 (2008) 1107-1109, DOI: 10.1002/cphc.200800065.