

Sample tube system for sequential *in situ* NMR studies of volatile and strongly adsorbed hydrocarbons

For investigating the conversion of heavy hydrocarbons on solids catalysts, a method was introduced consisting of a stepwise and separate study of volatile reaction products via gas-phase NMR and of strongly adsorbed reactants and reactions products using solid-state NMR. For this purpose, the solid catalyst loaded with the heavy hydrocarbons is placed in a glass tube consisting of two sections, which are separated by a glass wool layer. One of these sections contains the catalyst (**Fig. 1, right-hand side**), while the other section is empty (**Fig. 1, left-hand side**).

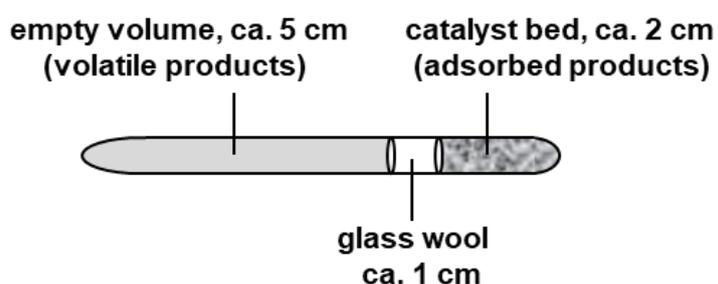


Fig. 1

After the catalytic conversion of the heavy hydrocarbons on the solid catalyst by heating the sealed sample tube, the volatile reaction products diffuse into the empty volume of the tube and can be investigated by ^1H spin-echo NMR spectroscopy using a liquid-state NMR probe (**Fig. 2**).

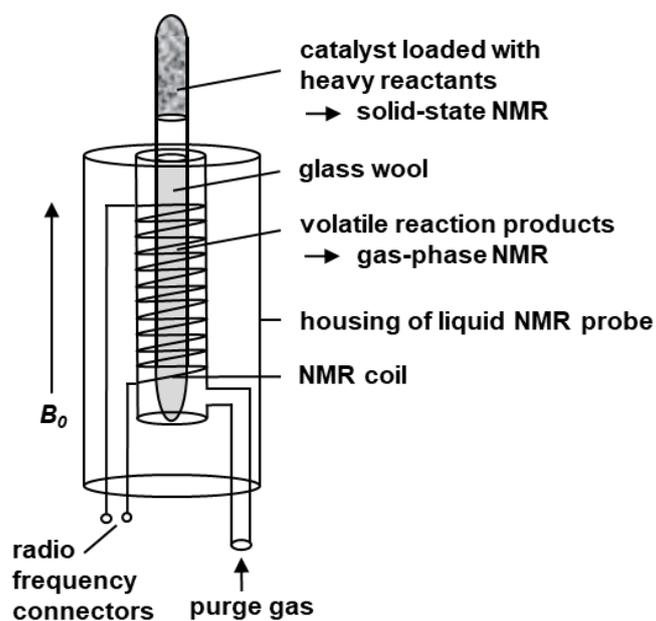


Fig. 2

Subsequently, the strongly adsorbed reaction products on the catalyst are studied via MAS NMR spectroscopy after transferring the reactant-loaded catalyst into an MAS NMR rotor without contact to air inside a mini glove box (see Section “mini glove box”), purged with dry nitrogen gas.

The catalyst bed in the sample tube in **Fig. 1** has a height of ca. 2 cm and is covered on top with a layer of glass wool with a height of ca. 1 cm. This tube is connected via quick-fits to a valve, like that described in Section “sample tube system 1”. After activation of the catalyst and adsorption of the reactants, an evacuation to ca. 2 mbar at room temperature within 1 min was performed and the sample tube was sealed in a length of 80 mm, which leads to an empty volume on top of ca. 5 cm.

In Ref. [1], this experimental approach was utilized for studying the reaction mechanism of the catalytic conversion of pure 2-ethylphenol (EtPh) on an acidic zeolite USY (bulk $n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.9). The EtPh conversion was performed by heating the sealed sample tube with the reactant-loaded catalyst at $T = 753$ K for 10 minutes. The study of the volatile reaction products in the empty volume of the sealed sample tube was performed using a 10 mm liquid-state Bruker NMR probe. The part containing the reactant-loaded catalyst was arranged outside of the NMR coil, as shown in **Fig. 2**. With this arrangement of the sealed sample tube, exclusively the volume containing the volatile reaction products was situated inside the NMR coil. For decreasing signals due to the NMR probe and adsorbed reactants in the catalyst bed, the ^1H NMR spectrum of the volatile reaction products was recorded using a $\pi/2$ - τ - π - τ -echo sequence. These measurements were performed at a Bruker Avance III 400WB spectrometer at the resonance frequency of $\nu_0 = 400.1$ MHz, with pulse lengths of $20 \mu\text{s}$ ($\pi/2$) and $40 \mu\text{s}$ (π), pulse delays τ of $470 \mu\text{s}$, and a repetition time of 20 s. ^1H NMR signals of water in the ambient air were suppressed by purging the inner part of the liquid-state NMR probe and the NMR coil with dry nitrogen gas (purge gas in **Fig. 2**).

In **Fig. 3a**, the ^1H spin-echo NMR spectrum recorded after conversion of 2-ethylphenol (EtPh) on the acidic zeolite USY at $T = 753$ K is shown. It consists of narrow signals indicating the high mobility of the volatile reaction products. These signals are due to CH_3 groups of the dealkylation products methane ($\delta_{\text{H}} = 0.2$ ppm) and ethane ($\delta_{\text{H}} = 0.9$ ppm) and CH_2 groups ($\delta_{\text{H}} = 1.3$ ppm) of propane and larger n-alkanes as well as formed water ($\delta_{\text{H}} = 4.0$ - 5.0 ppm), the latter caused by

a deoxygenation of EtPh. **Fig. 3b** shows the ^1H MAS NMR spectrum of the residual reactants and reactions product, which are strongly adsorbed on the zeolite. This spectrum consists of signals at $\delta_{1\text{H}} = 1.1$ ppm, 2.0 to 3.0 ppm, and 6.6 to 7.0 ppm, which are caused by CH_3 and CH_2 groups and hydrogen atoms of the aromatic ring of EtPh, respectively. The strong broadening of these signals is due to homonuclear dipole-dipole interactions.

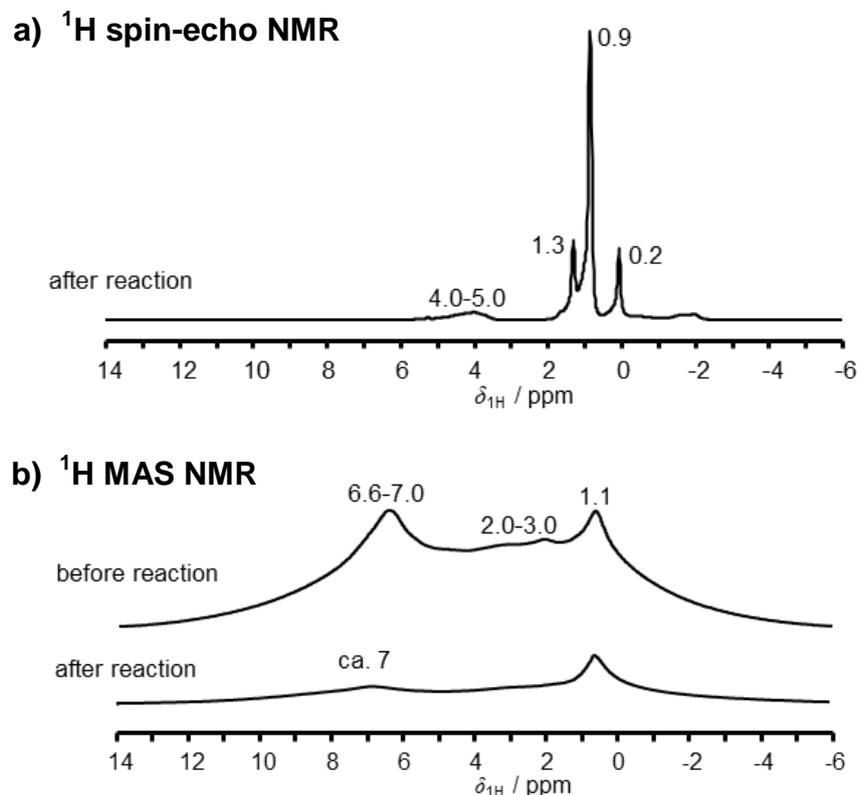


Fig. 3

The ^{13}C CP MAS NMR spectra of the reactants before the catalytic conversion of 2-ethylphenol (EtPh) and of the strongly adsorbed reaction products after the conversion (**Fig. 4** and Fig. 2c of Ref. [1]) support the deoxygenation of EtPh, responsible for the water signal at $\delta_{1\text{H}} = 4$ to 5 ppm in the ^1H spin-echo NMR spectrum in **Fig. 3a**. After the conversion, the ^{13}C CPMAS NMR signal of ipso carbon atoms at $\delta_{13\text{C}} = 154$ ppm is absent. A ^{13}C CPMAS NMR signal at $\delta_{13\text{C}} = 21$ ppm, due to the CH_3 groups bound to aromatics, and a signal shoulder at $\delta_{13\text{C}} = 138$ ppm indicate the formation of toluene. ^{13}C CPMAS NMR signals at $\delta_{13\text{C}} = 126$ to 129 ppm are caused by common aromatic carbon atoms, such as in toluene and

polyaromatics. Hence, the combined application of ^1H spin-echo NMR and solid-state NMR spectroscopy evidenced the deoxygenation of EtPh and the formation of light alkanes, such as methane, ethane, and propane by dealkylation of this reactant [1].

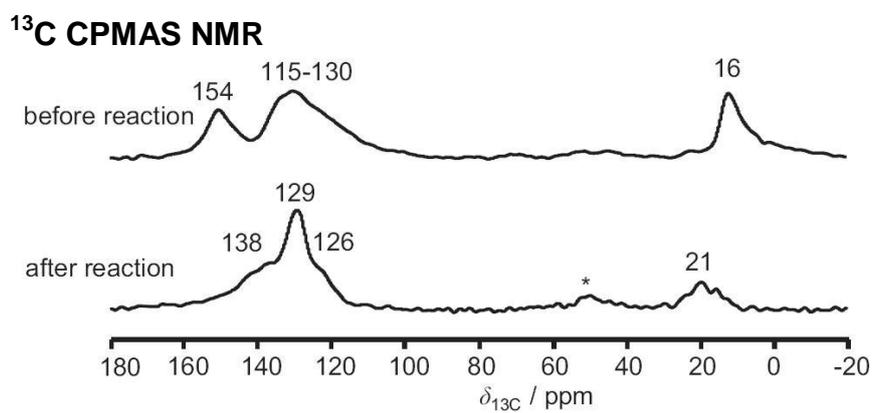


Fig. 4

Reference:

- [1] S. Lang, M. Dyballa, Y. Traa, D. Estes, E. Klemm, M. Hunger, *Direct proof of volatile and adsorbed hydrocarbons on solid catalysts by complementary NMR methods*, *Chemie Ingenieur Technik* 93 (2021) 1020-1023, DOI: 10.1002/cite.202000128.