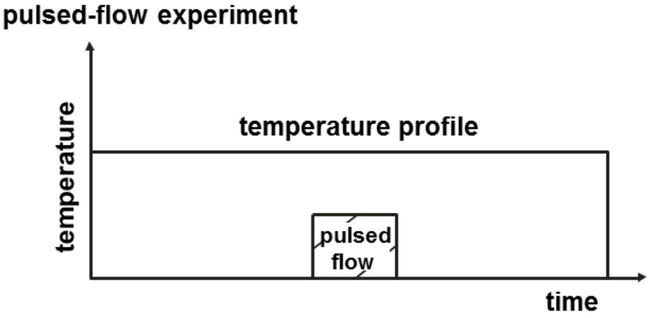
Combined *in situ* solid-state NMR and UV/Vis studies of heterogeneously catalyzed reactions under pulsed-flow conditions

Spectroscopic background: In the *in situ* pulsed-flow solid-state NMR experiment shown in **Scheme 1** (Fig. 7d in Ref. [1]), the catalyst sample inside the MAS NMR rotor is heated at elevated and constant temperature and, for a short duration, a pulse of liquid reactants is injected into the spinning MAS NMR rotor. Subsequently, the catalytic reaction or the isotopic exchange of reactants on the solid catalyst is investigated as a function of time. The pulsed-flow experiment is **useful for time-resolved investigations of rapid reactions** of the injected compounds with a well-defined start time.



Scheme 1

The equipment is a combination of an *in situ* flow MAS NMR probe and a micro-pulse pump (see Section “equipment 2” via link “*In Situ* Solid-State NMR Techniques”). In some cases, an *in situ* UV/Vis spectrometer is coupled via glass fibre optics (see Section “flow probe 3” via link “*In Situ* Solid-State NMR Techniques”).

In **Fig. 1**, a typical application of the *in situ* pulsed-flow MAS NMR technique combined with *in situ* UV/Vis spectroscopy is demonstrated [4]. The *in situ* ^{1}H MAS NMR and UV/Vis spectra were **recorded after injection of ethyl-d$_5$-benzene at T = 393 to 523 K on a dehydrated zeolite deH-Y** (**Fig. 1, left-hand side**). The ^{1}H MAS NMR signals at δ_{1H} = 1.2 ppm, 2.7 ppm, and 7.3 ppm arise from hydrogen atoms in side-chain methyl and methylene groups and in the non-deuterated aromatic rings, respectively, of ethyl-d$_5$-benzene (asterisks are spinning sidebands). The signals of non-deuterated bridging OH groups (Si(OH)Al) acting as Broensted acid sites of the zeolite deH-Y are too weak and broad to be observed under the applied conditions. Simultaneously recorded *in situ* UV/Vis spectra (right) consist of bands at λ = 270 and 400 nm due to neutral aromatics (ethylbenzene) and ethylcyclohexadienyl carbenium ions, respectively (**Fig. 1, right-hand side**).

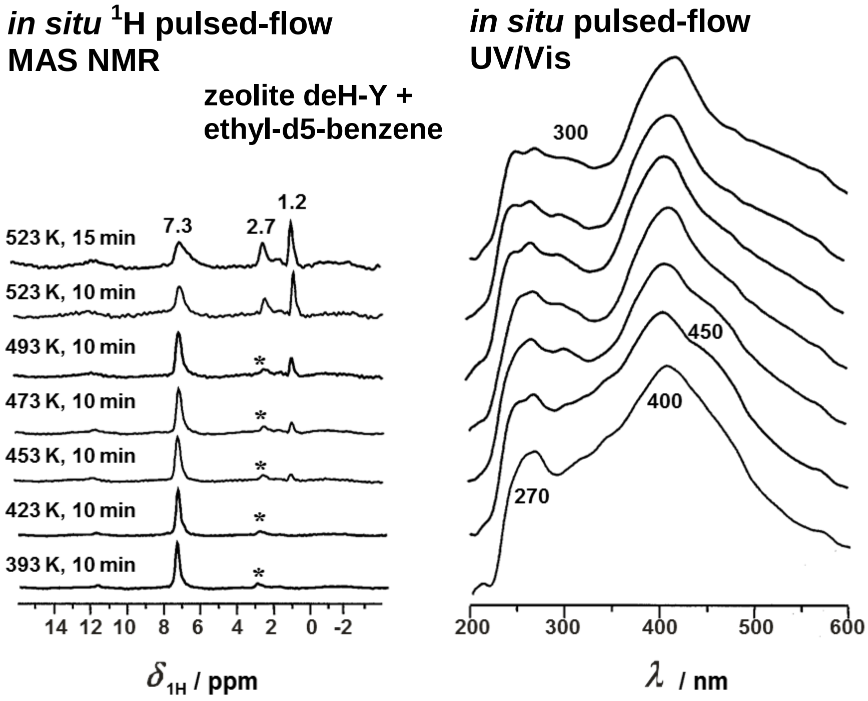


Fig. 1

The time-dependent evaluation of the ^{1}H MAS NMR signal at δ_{1H} = 1.2 ppm (**Fig. 2, left-hand side**) gave an activation energy for the H/D exchange at the side-chain of 194 kJ/mol (**Fig. 2, right-hand side**). This regioselective H/D exchange at the side-chain of ethylbenzene on dehydrated zeolite deH-Y and the determined activation energy was explained by the formation of *sec*-ethylphenyl carbenium ions.

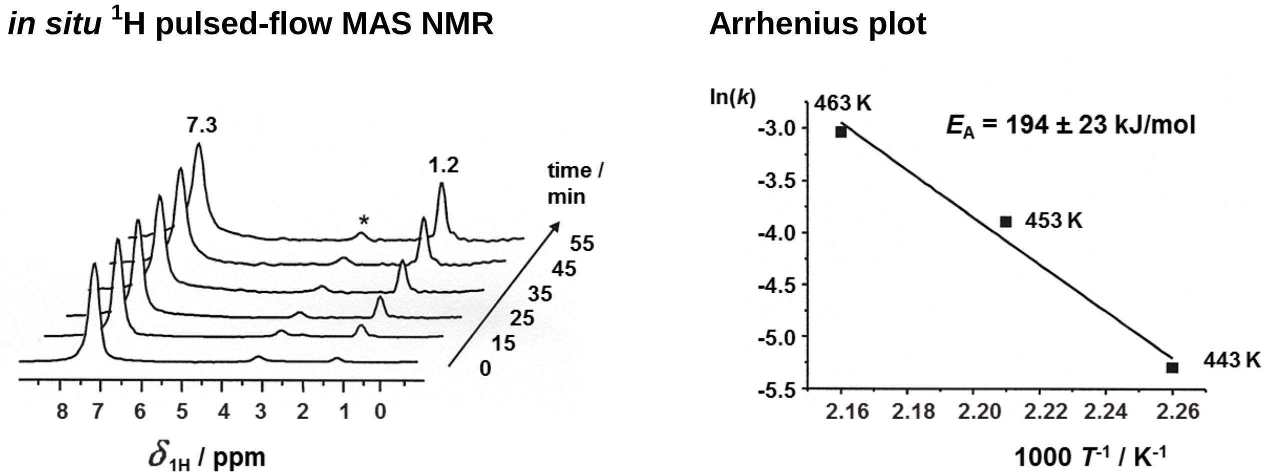
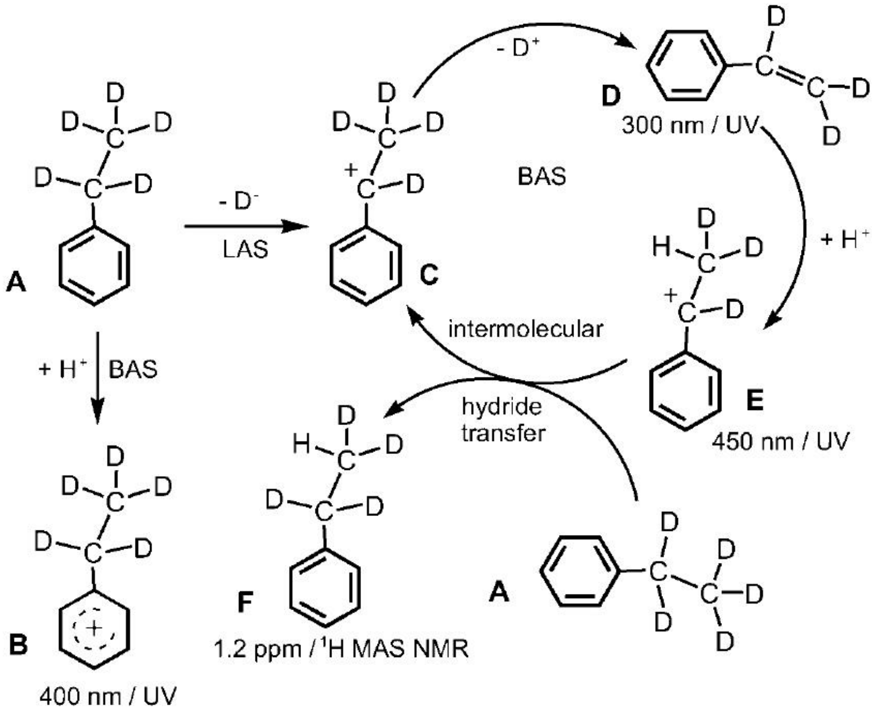


Fig. 2

Based on the experimental results of *in situ* pulsed-flow MAS NMR and UV/Vis studies, the mechanism of the regioselective H/D exchange in **Scheme 2** was suggested. In the case of adsorption of **A** at Broensted acid sites (BAS) of zeolite deH-Y, **A** is directly protonated to the ethylcyclohexadienyl carbenium ion **B**. The formation of **B** is indicated by the UV/Vis band at λ = 400 nm. Adsorption of **A** at Lewis acid sites (LAS) causes a hydride abstraction leading to the sec-ethylphenyl carbenium ion **C**. Deprotonation of **C** causes the formation of styrene **D** as an intermediate, which is followed by protonation leading to the sec-ethylphenyl carbenium ion **E**. This carbenium ion has a significant lifetime because it has to climb the energy barrier of the subsequent hydride transfer. **C** and **E** are carbenium ions of the same type and observable as UV/Vis bands at λ = 450 nm. Due to low number of Broensted acid sites per supercage (< 1 SiOHAl/s.c.), the styrene molecule **D** cannot be rapidly protonated by another Broensted acid site in the vicinity and results in the weak UV/Vis bands at λ = 300 nm.



Scheme 2

Catalyst preparation: The dealuminated zeolite deH-Y (n_{Si}/n_{Al} = 5.4) was obtained by steaming zeolite H-Y (n_{Si}/n_{Al} = 2.7), leading to a material with extra-framework aluminum species, which act as Lewis acid sites. Before the use of zeolite deH-Y for *in situ* pulsed-flow experiments, the sample material was dehydrated in a glass tube connected with a vacuum line (see “sample tube system 1” and “vacuum line 1” via link “*In Situ* Solid-State NMR Techniques”). This treatment starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to T = 723 K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line is ventilated with air. The transfer of the dehydrated sample into the MAS NMR rotor is performed without air contact, e.g., in a glove box purged with dry nitrogen gas (see Section “mini glove box” via link “*In Situ* Solid-State NMR Techniques”).

In situ studies: The *in situ* ^{13}C stopped-flow MAS NMR spectra in Figs. 1 and 2 were recorded using the equipment described in Section “equipment 2” and a 7 mm high-temperature MAS NMR probe of Doty Scientific Instruments, modified as described in Section “flow probe 3”, both accessible via link “*In Situ* Solid-State NMR Technique”.

Prior to the *in situ* experiments, ca. 100 mg of dehydrated zeolite deH-Y were filled into an MAS NMR rotor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the MAS NMR probe without contact to air, the zeolite sample was additionally treated at T = 573 K for 1 h under a flow of dry nitrogen and then kept at the chosen reaction temperature. Subsequently, a pulse of 7.8 mg ethyl-d5-benzene (deuterated ethyl groups, deuteration degree of 99.3%, Dr. Ehrenstorfer GmbH, Germany) was injected into the 7 mm MAS NMR rotor using a micro pump (see “equipment 2”). The loading of the zeolite deH-Y obtained by this way was adjusted to ca. 1 ethyl-d5-benzene per supercage. For the quantitative evaluation of H/D exchange kinetics, the ^{1}H MAS NMR signal of hydrogen atoms at the non-deuterated benzene rings (signal at δ_{1H} = 7.3 ppm) was utilized as internal intensity standard. The *in situ* ^{1}H pulsed-flow MAS NMR spectra were recorded at the resonance frequency of ν_0 = 400.1 MHz with a repetition time of 8 s.

At the bottom of the 7 mm MAS NMR rotor, a quartz glass window was installed. Via this quartz glass window and using a glass fiber optics, the catalyst inside the rotor was investigated by a fiber-optic UV/Vis spectrometer. Reference UV/Vis spectra of calcined zeolite deH-Y were recorded at the reaction temperature prior to introducing reactants. *In situ* UV/Vis measurements between λ = 200 and 600 nm in the diffuse reflection mode were conducted with an HPSUV1000A Fiber Optic spectrometer, an AvaLight-DH-S deuterium light source, and a glass fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes.

References:

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[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.

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[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.