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 reactants with a well-defined start time.





The equipment is a combination of an *in situ* flow MAS NMR probe and a micro-pulse pump (see Section "equipment 2", accessible via link "*In Situ* Solid-State NMR Techniques"). In some cases, an *in situ* UV/Vis spectrometer was coupled with the *in situ* MAS NMR probe via a fibre optics (see Section "flow probe 3", accessible 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* ¹H 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 ¹H MAS NMR signals at $\delta_{1H} = 1.2$ 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-d₅-benzene (the asterisks are spinning sidebands). The signals of non-deuterated bridging OH groups (Si(OH)AI), acting as Broensted acid sites of the zeolite deH-Y, are too weak and broad to be observed under the experimental

conditions. Simultaneously recorded *in situ* UV/Vis spectra (right) consist of bands at $\lambda = 270$ and 400 nm due to neutral aromatics (ethylbenzene) and ethylcyclohexadienyl carbenium ions, respectively (**Fig. 1, right-hand side**).





The evaluation of the ¹H MAS NMR signal at $\delta_{1H} = 1.2$ ppm (**Fig. 2, left-hand side**) as a functions of time gave an activation energy for the H/D exchange at the sidechain of $E_A = 194$ 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.







Based on the experimental results of *in situ* pulsed-flow MAS NMR and *in situ* UV/Vis studies, the mechanism of the regioselective H/D exchange in **Scheme 2** was suggested. In the case of adsorption of ethyl-d5-benzene **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 $\lambda = 400$ nm. Adsorption of **A** at Lewis acid sites (LAS) causes a hydride abstraction leading to the sec-ethylphenyl carbenium ion **C**. Deprotonation of **C** leads to the formation of styrene **D** as an intermediate, which is followed by a protonation causing the formation of the sec-ethylphenyl carbenium ion **E**. This carbenium ion **E** 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 $\lambda = 450$ nm. Due to low number of Broensted acid sites per supercage (< 1 SiOHAI/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 $\lambda = 300$ nm.



Scheme 2

An alternative experimental approach combining reactant pulses with solid-state NMR spectroscopy utilizes a catalytic equipment (*ex situ*) with a flow reactor, which

can be quenched from reaction temperature to room temperature in a short time [5, 6]. Using this equipment, a short (e.g. 0.2 s to 16 s) reactant pulse was injected into the catalyst bed inside the flow reactor, which was preheated at reaction temperature. After a well-defined time, the reaction was quenched to room temperature (T = 298 K). Subsequently, the catalyst bed was isolated and transferred into an MAS rotor, which was sealed with a gas-tight rotor cap in a glove box at room temperature. Then, the MAS rotor was inserted into a common MAS NMR probe and the reactants on the catalyst were measured by ¹³C MAS NMR spectroscopy at low temperature (T = 77 K). This pulse-quench technique was applied for investigating the reactions of acetone (5] and methanol [6] on zeolite H-ZSM-5.

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 acting as Lewis acid sites. Before the use of zeolite deH-Y for *in situ* pulsed-flow experiments, the sample material was dehydrated in a "sample tube system 1" at "vacuum line 1" (see Sections "sample tube system 1" and "vacuum line 1", accessible 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 was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system was 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 in a glove box (see Section "mini glove box", accessible via link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas.

In situ studies: The *in situ* ¹³C 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. Subsequently, the MAS rotor was closed with a rotor cap containing a

hole in the center. 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 flowing dry nitrogen gas 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 the H/D exchange kinetics, the ¹H MAS NMR signal of hydrogen atoms at the non-deuterated benzene rings ($\delta_{1H} = 7.3$ ppm) was utilized as internal intensity standard. The *in situ* ¹H pulsed-flow MAS NMR spectra were recorded at a Bruker MSL 400WB spectrometer with a resonance frequency of $v_0 = 400.1$ MHz, a sample spinning rate of $v_{rot} \cong 2$ kHz, and using 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 fiber optics, the catalyst inside the rotor was investigated by a fiber optics UV/Vis spectrometer (see "flow probe 3"). Prior to introducing the reactants, reference UV/Vis spectra of the calcined zeolite deH-Y were recorded at the reaction temperature. The *in situ* UV/Vis measurements were performed between $\lambda = 200$ and 600 nm in the diffuse reflection mode with an HPSUV1000A Fiber Optics spectrometer, an AvaLight-DH-S deuterium light source, and a fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes.

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