In situ solid-state NMR studies of heterogeneously catalyzed reactions under stopped-flow conditions

Spectroscopic background: With the development and introduction of *in situ* flow MAS NMR probes (see Refs. [1] and [2] and Topic "3" of link "*In Situ* Solid-State NMR Techniques"), stopped-flow experiments by utilizing solid-state NMR became possible [3-6]. **Fig. 1** shows one of the **different protocols of stopped-flow experiments** for the study of reaction mechanisms in the research field of heterogeneous catalysis [4] (see also Fig. 7 in Ref. [2]). This protocol consists of periods (a) to (c) with different reaction temperatures, but a continuous flow of reactants. If during (a) to (c) specific surface compounds are formed on the catalyst, their behavior in period (c) of the **stopped-flow experiment decides, whether surface compounds are intermediates or chemically stable by-products** of the reaction under study. For demonstrating the performance of an *in situ* stopped-flow MAS NMR experiment, the investigation of the methylation of aniline with ^{13}C-methanol to N-methylaniline on a basic zeolite Cs,Na-Y/CsOH was chosen [4]. For further information on zeolite Cs,Na-Y/CsOH, see Section "method 11" via the link "*In Situ* Solid-State NMR Techniques".

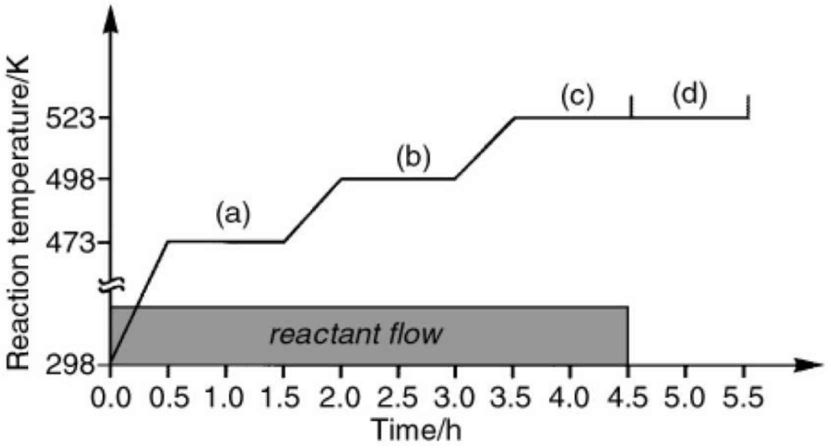

Fig. 1

N-methylaniline is an important chemical product applied as a latent and coupling solvent and is also utilized as an **intermediate for dyes, agrochemicals and other organic products manufacturing**. Furthermore, it a non-traditional **antiknock agent** increasingly used by petroleum refiners and fuel distributors around the world to increase the octane number of gasoline petrol. Traditionally, N-methylaniline is produced by the reaction of aniline and methanol in the presence of sulfuric acid or hydrochloric acid as catalysts, which are very corrosive liquids. Alternative approaches are the reaction of aniline with methanol or formaldehyde on oxides, clays, and zeolites [7-9]. Therefore, the mechanism of this reaction on cesium-containing zeolite Y was a topic of research [4, 11-14].

According to the reaction mechanism described by Equs. (1) to (3) [4], **aniline ($C_6H_5NH_2$) reacts with formaldehyded ($H^{13}CHO$)**, which is formed by dehydrogenation of methanol. In the *in situ* stopped-flow MAS NMR experiments, ^{13}C-enriched methanol, $^{13}CH_3OH$, is used. In the subsequent reaction step (Equ. (3)), the N-methyleneaniline, formed via Equ. (2), is dehydrogenated to N-methylaniline.

$$^{13}CH_3OH\ (\delta_{13C} = 49\ \text{ppm}) \rightarrow H^{13}CHO + H_2 \tag{1}$$

$$C_6H_5NH_2 + H^{13}CHO \rightarrow C_6H_5N{=}^{13}CH_2\ (\delta_{13C} = 157\ \text{ppm}) + H_2O \tag{2}$$

$$C_6H_5N{=}^{13}CH_2\ (\delta_{13C} = 157\ \text{ppm}) + H_2 \rightarrow C_6H_5NH^{13}CH_3\ (\delta_{13C} = 29\ \text{ppm}) \tag{3}$$

Figs. 2a to c, left, show the *in situ* ^{13}C stopped-flow MAS NMR spectra obtained during the conversion of pure ^{13}C-methanol on zeolite Cs,Na-Y/CsOH at reaction temperatures of T = 473 to 523 K under steady-state conditions (compare **Fig. 1**) [4]. The signal at δ_{13C} = 49 ppm is due to adsorbed methanol molecules. With increasing reaction temperature, a second signal appears at δ_{13C} = 166 ppm, which is caused by surface formate species [15].

Figs. 2a to 2c, right, show the ***in situ* ^{13}C stopped-flow MAS NMR spectra recorded during conversion of the aniline/^{13}C-methanol mixture on zeolite Cs,Na-Y/CsOH** at reaction temperatures of T = 473 to 523 K [4]. While the spectrum obtained at T = 473 K consists of a single signal due to methanol molecules at δ_{13C} = 49 ppm, in the spectrum obtained at T = 498 K additional signals occur at δ_{13C} = 29 and 157 ppm. The signal at δ_{13C} = 29 ppm is due to the reaction product N-methylaniline while the signal at δ_{13C} = 157 ppm hints to the formation of N-methyleneaniline [16]. Further increase of the reaction temperature to T = 523 K leads to the formation of surface formate species at δ_{13C} = 166 ppm and a strong increase of the signal at δ_{13C} = 29 ppm due to the reaction product N-methylaniline.

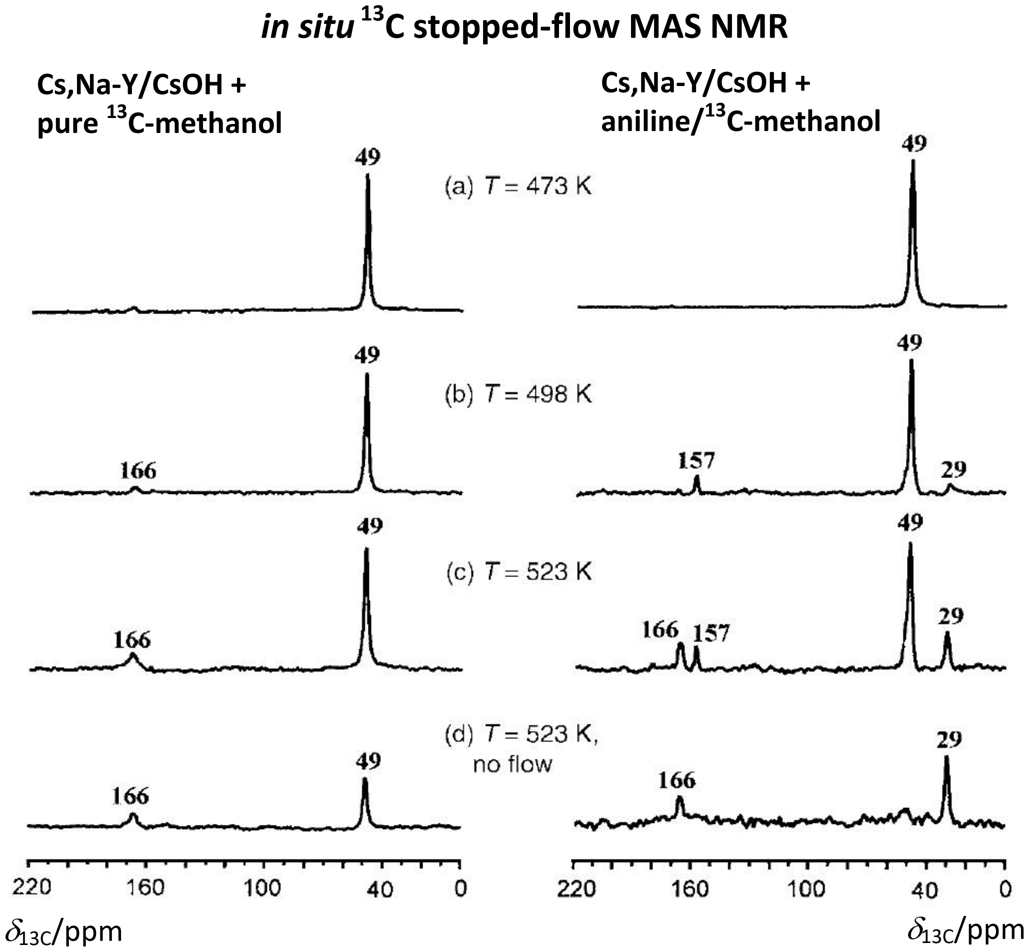

Fig. 2

To decide whether the N-methyleneaniline species at δ_{13C} = 157 ppm are chemically stable by-product, like “spectators” of the reaction, reactive intermediates, a stopped-flow experiment was performed. For this purpose, the reactant flow was suddenly stopped after period (c) of the protocol in **Fig. 1**, and a spectrum was recorded while keeping the temperature at T = 523 K. In the corresponding spectrum in **Fig. 2d**, right, the signal at δ_{13C} = 166 ppm remained constant. On the other hand, the signals of methanol at δ_{13C} = 49 ppm and of N-methyleneaniline at δ_{13C} = 157 ppm disappeared completely, while the signal of the reaction product N-methylaniline at δ_{13C} = 29 ppm gained significantly in intensity. Hence, not only ^{13}C-methanol, but also the N-methyleneaniline species are consumed by the formation of N-methylaniline. This finding indicates that the N-**methyleneaniline species occurring at δ_{13C} = 157 ppm play a role of an intermediate** in the methylation of aniline.

Catalyst preparation: The zeolite CsOH/Cs,Na-Y used as catalyst in the present work has an n_{Si}/n_{Al} ratio of 2.6 and was prepared as described elsewhere [17]. After the sodium to cesium exchange up to a exchange degree of 70%, zeolite Cs,Na-Y was impregnated with an aqueous solution of cesium hydroxide, such as to arrive at a loading of 14 CsOH per unit cell. Subsequently, the material was calcined for 12 h at T = 723 K and sealed in a glass tube, until the use of this catalyst for an *in situ* experiment.

In situ solid-state NMR studies: The *in situ* ^{13}C stopped-flow MAS NMR spectra in Fig. 2 were recorded using the equipment described in the Section “equipment 1” 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”.

After filling the calcined catalyst into the MAS rotor inside a mini glove box purged with dry nitrogen gas (see Section “mini glove box”) and transferring the rotor into the spectrometer without contact to air, the temperature was raised to T = 473 K, 498 K, and 523 K, while the carrier gas (nitrogen) loaded with the reactants was flowing. In all experiments, a ^{13}C-methanol flow according to a modified residence time of W/F = 40 g·h·mol^{-1} (m_{cat} = 250 mg, ^{13}C-methanol flow of 6.25 mmol·h^{-1}) was used. The molar ratio of ^{13}C-methanol to aniline (the latter with natural ^{13}C-abundance) mixture was 4 to 1. The *in situ* ^{13}C stopped-flow NMR measurements were performed at the resonance frequency of ν_{rot} = 100.4 MHz, with direct $\pi/2$ pulse excitation, a repetition time of 5 s and ca. 500 scans per spectrum. After recording the spectra under steady-state conditions at reaction temperatures of T = 473 K, 498 K and 523 K, the reactant flow was stopped, and the further conversion of the adsorbate compounds was observed without purging the catalyst.

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