

***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 were 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] (Fig. 7 in Ref. [2]). This protocol consists of periods (a) to (c) with different reaction temperatures during a continuous flow of gaseous reactants. If surface species are formed on the catalyst in periods (a) to (c), their behavior in period (d) of the **stopped-flow experiment decides, whether these surface species 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 (for information on zeolite Cs,Na-Y/CsOH, see Section “method 16”) [4].

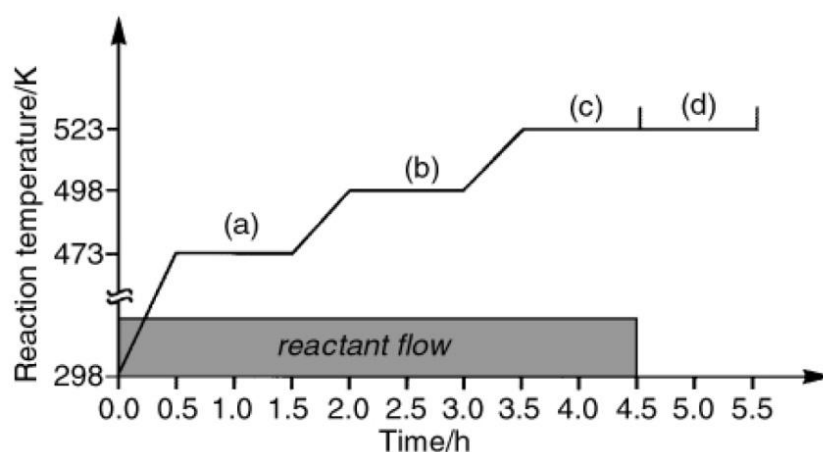
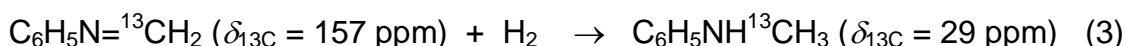
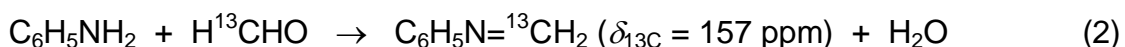
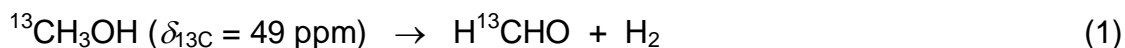


Fig. 1

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 is 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 in the focus of topic [4, 11-14].

According to the reaction mechanism described by Eqs. (1) to (3) [4], **aniline ($\text{C}_6\text{H}_5\text{NH}_2$) 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 ($^{13}\text{CH}_3\text{OH}$) was used. In the subsequent reaction step (Eq. (3)), the N-methyleneaniline, formed via Eq. (2), is dehydrated to N-methylaniline.



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 (**Fig. 1**) [4]. The signal at $\delta_{^{13}\text{C}} = 49$ ppm is due to adsorbed methanol molecules. With increasing reaction temperature, a second signal appears at $\delta_{^{13}\text{C}} = 166$ 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 $\delta_{^{13}\text{C}} = 49$ ppm, in the spectrum obtained at $T = 498$ K additional signals occur at $\delta_{^{13}\text{C}} = 29$ and 157 ppm. The signal at $\delta_{^{13}\text{C}} = 29$ ppm is due to the reaction product N-methylaniline, while the signal at $\delta_{^{13}\text{C}} = 157$ 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 $\delta_{^{13}\text{C}} = 166$ ppm and a strong increase of the signal at $\delta_{^{13}\text{C}} = 29$ ppm due to the reaction product N-methylaniline.

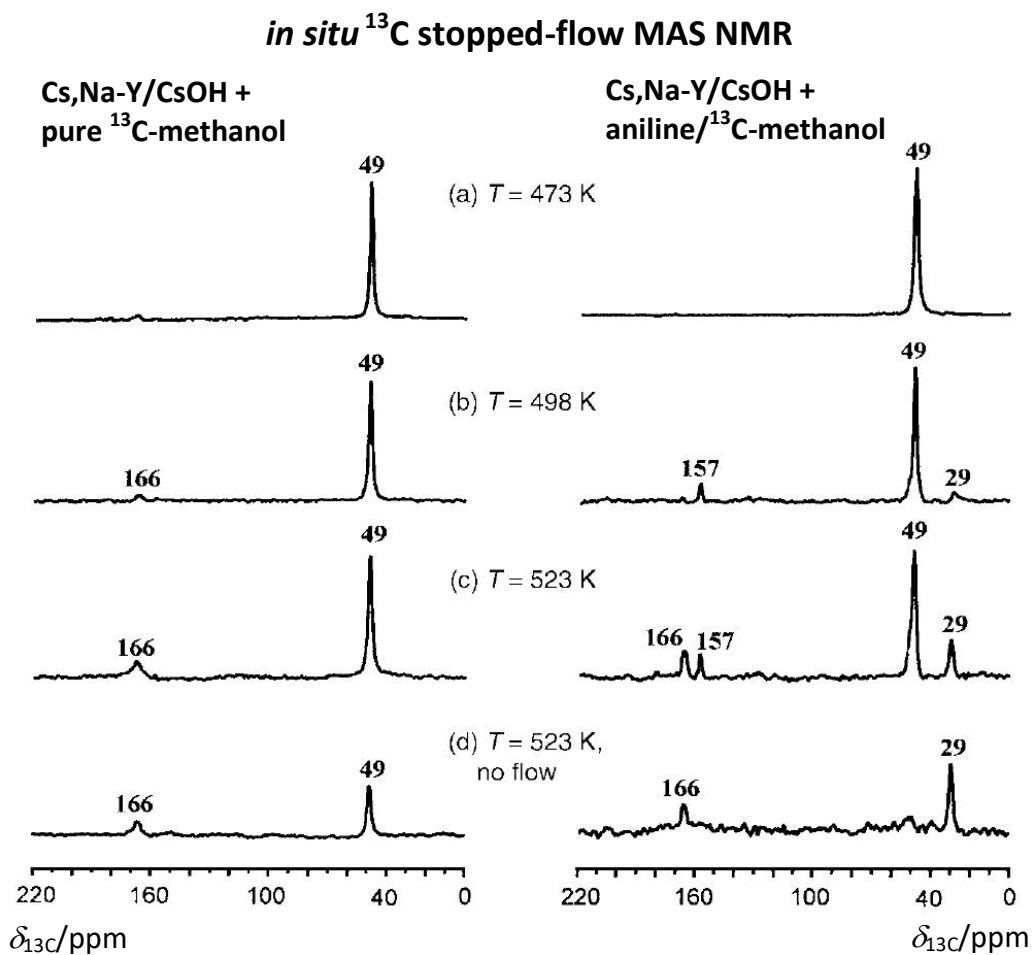


Fig. 2

To decide whether the N-methylenedianiline species at $\delta_{13\text{C}} = 157\text{ ppm}$ are chemically stable by-products, 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 $T = 523\text{ K}$ during period (d). In the corresponding spectrum in **Fig. 2d**, right, the signal at $\delta_{13\text{C}} = 166\text{ ppm}$ remained constant. On the other hand, the signals of methanol at $\delta_{13\text{C}} = 49\text{ ppm}$ and of N-methylenedianiline at $\delta_{13\text{C}} = 157\text{ ppm}$ disappeared completely, while the signal of the reaction product N-methylaniline at $\delta_{13\text{C}} = 29\text{ ppm}$ gained significantly in intensity. Hence, not only ^{13}C -methanol, but also the N-methylenedianiline species are consumed by the formation of N-methylaniline. This finding indicates that the **N-methylenedianiline species occurring at $\delta_{13\text{C}} = 157\text{ ppm}$ 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 study has a $n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.6 and was prepared as described elsewhere [17]. After the sodium to cesium exchange up to an exchange degree of 70%, the obtained zeolite Cs,Na-Y was impregnated with an aqueous solution of cesium hydroxide 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 (see Section “mini glove box”, accessible via link “*In Situ* Solid-State NMR Techniques”), purged with dry nitrogen gas, the MAS rotor was closed with a rotor cap containing a hole in the center. Upon 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 injected. In all experiments, a ^{13}C -methanol flow according to a modified residence time of $W/F = 40 \text{ g}\cdot\text{h}\cdot\text{mol}^{-1}$ ($m_{\text{cat}} = 250 \text{ mg}$, ^{13}C -methanol flow of $6.25 \text{ mmol}\cdot\text{h}^{-1}$) 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 a Bruker MSL 400WB spectrometer with the resonance frequency of $\nu_0 = 100.4 \text{ MHz}$, a sample spinning rate of $\nu_{\text{rot}} \cong 2.5 \text{ kHz}$, upon 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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