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In situ stopped-flow (SF) MAS NMR spectroscopy: a novel NMR technique applied for the study of aniline methylation on a solid base catalyst

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By the novel *in situ* stopped-flow MAS NMR technique allowing the observation of adsorbates on a solid catalyst after stopping the continuous reactant flow, *N*-methyleneaniline was identified as an intermediate in the formation of *N*-methylaniline by methylation of aniline with methanol on a basic CsOH/Cs,Na-Y zeolite.

In the past decade, *in situ* MAS NMR spectroscopy has been developed as a powerful tool for investigating heterogeneously catalyzed reactions.[1] Since 1995, a number of new *in situ* MAS NMR techniques have been developed allowing the study of reactions under continuous flow conditions.[2] With these techniques, a direct NMR investigation of the formation and transformation of surface compounds under steady-state conditions and a simultaneous gas chromatographic analysis of the reaction products are possible. In the present communication we report on the application of a new *in situ* stopped-flow (SF) MAS NMR experiment which is suitable to determine intermediates of heterogeneously catalyzed reactions. With this method, an intermediate involved in aniline methylation on basic zeolite CsOH/Cs,Na-Y under flow conditions was determined for the first time.

The zeolite CsOH/Cs,Na-Y used as catalyst in the present work had an $n_{\mathrm{Si}}/n_{\mathrm{Al}}$ ratio of 2.6 and was prepared as described elsewhere.[3] After the sodium/caesium exchange (sodium exchange degree of 70%), zeolite Cs,Na-Y was impregnated with an aqueous solution of caesium hydroxide such as to arrive at a loading of 14 CsOH per unit cell. Subsequently, the material was calcined for 12 h at 723 K. The NMR experiments were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 100.4 MHz, with direct excitation ($\pi/2$ pulse), a repetition time of 5 s and *ca*. 500 scans per spectrum. For the *in situ* measurements, the equipment described in ref. 2(*f*) and a modified 7 mm high-temperature Doty MAS NMR probe were used. The protocol of the 'stopped-flow' experiment is shown in Fig. 1. After filling the calcined catalyst into the MAS rotor and transferring the rotor into the spectrometer, the temperature was raised to 473, 498 and 523 K while the carrier gas (nitrogen) loaded with the reactants was flowing. In all experiments, a methanol (^{13}C-enriched) flow according to a modified residence time of $W/F = 40\ \mathrm{g\ h\ mol^{-1}}$ ($m_{\mathrm{cat}} = 250$ mg, $\dot{n}_{\mathrm{me}} = 6.25$ mmol h^{-1}) was used. The molar ratio of the methanol–aniline (natural ^{13}C-abundance) mixture was 4 : 1. After recording the ^{13}C MAS NMR spectra under steady-state conditions at reaction temperatures of 473, 498 and 523 K, the reactant flow was stopped, and the further conversion of the adsorbate compounds was observed, without purging the catalyst (see Fig. 1).

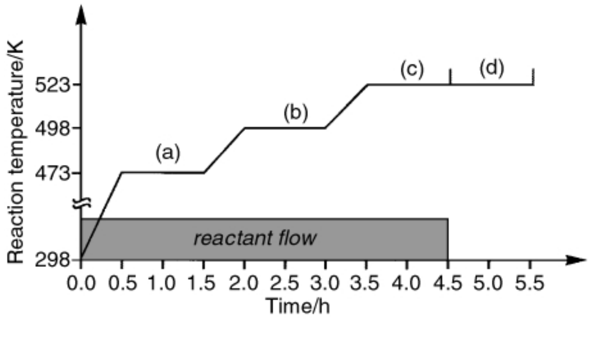

Fig. 1 Protocol of the *in situ* SF MAS NMR experiment consisting of periods (a) to (c) for the study of heterogeneously catalyzed reactions under steady-state conditions at different temperatures and a period (d), in which the consecutive conversion of previously formed compounds can be investigated.

Methanol was applied as methylating agent, and the conversion of this reactant alone on zeolite CsOH/Cs,Na-Y was investigated in the first experiments. Fig. 2(a)–(c), left, show the *in situ* ^{13}C MAS NMR spectra obtained at reaction temperatures of 473–523 K under steady-state conditions. The signal at 49 ppm is due to adsorbed methanol molecules. With increasing reaction temperature, a second signal appears at 166 ppm which is caused by surface formate species.[4] In an earlier work on methylation of toluene on a basic zeolite CsOH/Cs,Na-X it was shown that surface formate species occurring at 166 ppm are consumed by the reaction which indicates that these species can act as methylating agents.[4c] The ^{13}C MAS NMR spectrum recorded immediately after stopping the methanol flow at 523 K shows a significant decrease of the methanol signal at 49 ppm and only a weak decrease of surface formate species at 166 ppm [Fig. 2(d), left]. This indicates that the surface formate species are quite stable at 523 K.

Fig. 2(a)–(c), right, show the ^{13}C MAS NMR spectra recorded during conversion of the methanol–aniline mixture on zeolite CsOH/Cs,Na-Y at reaction temperatures of 473–523 K. While the spectrum obtained at 473 K consists only of a single signal due to methanol molecules at 49 ppm, in the spectrum obtained at 498 K additional signals occur at 29 and 157 ppm. The signal at 29 ppm is due to the reaction product *N*-methylaniline.[5] The signal at 157 ppm can be assigned to *N*-methyleneaniline, based on work by Kamachi and coworkers who observed a signal at *ca*. 155 ppm in the ^{13}C NMR spectrum of *N*-methyleneaniline in THF-d$_8$.[6] Further increase of the reaction temperature to 523 K leads to the formation of surface formate species at 166 ppm and a strong increase of the signal at 29 ppm due to the reaction product *N*-methylaniline.

To find out whether the *N*-methyleneaniline species at 157 ppm is an intermediate in the formation of *N*-methylaniline on zeolite CsOH/Cs,Na-Y, a stopped-flow experiment was performed: the reactant flow was suddenly stopped, and a spectrum was recorded while keeping the temperature at 523 K. In the spectrum obtained [Fig. 2(d), right], the signal at 166 ppm remained constant. On the other hand, the signals of methanol at 49 ppm and of *N*-methyleneaniline at 157 ppm disappeared completely, while the signal of the reaction product *N*-methylaniline at 29 ppm gained significantly in intensity. Hence, not only methanol, but also the *N*-methyleneaniline species are consumed by the formation of *N*-methylaniline. This finding indicates that the *N*-methyleneaniline species occurring

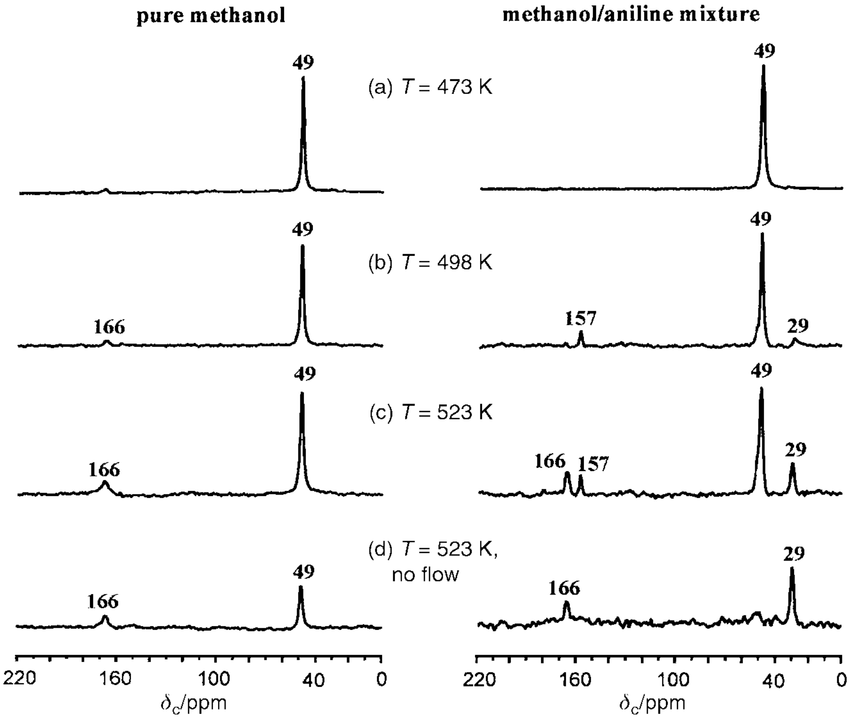

Fig. 2 *In situ* ^{13}C MAS NMR spectra obtained during the conversion of pure methanol (left) and a methanol–aniline mixture (right) on zeolite CsOH/Cs,Na-Y under flow conditions (W/F = 40 g h mol^{-1}) at reaction temperatures of 473 (a), 498 (b) and 523 K (c) and after stopping the reactant flow at 523 K (d).

at 157 ppm acts as an intermediate in the methylation of aniline.

The detection of *N*-methyleneaniline as an intermediate species can be accounted for by a mechanistic pathway which includes dehydrogenation of methanol to formaldehyde, [eqn. (1)], condensation of aniline with formaldehyde leading to *N*-methyleneaniline [eqn. (2)] and hydrogenation of *N*-methyleneaniline to *N*-methylaniline by H_2 produced during the methanol dehydrogenation [eqn. (3)]:

$$^{13}CH_3OH \text{ (49 ppm)} \rightarrow H^{13}CHO + H_2 \qquad (1)$$

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

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

Based on the results of the present study we cannot decide whether the formate species observed at 166 ppm, or formaldehyde directly formed by conversion of methanol, acts as the methylating agent in the first reaction step. Our previous results demonstrated that the formation of formate species and aniline alkylation are parallel, *i.e.*, competing reactions on basic zeolites and that formate species most probably do not participate in the alkylation.[8] The fact that we did not observe formaldehyde species in the *in situ* MAS NMR experiments is due to its high reactivity on basic zeolites and, consequently, can be explained by a higher rate of reaction (2) compared to reaction (3).

It should be mentioned that the mechanism proposed for aniline alkylation in the present study is consistent with those suggested previously for side-chain alkylation of toluene on basic zeolites.[4b,7] Furthermore, it is also in line with the mechanism proposed on the basis of a recent *in situ* MAS NMR spectroscopic study of aniline methylation performed under batch conditions.[8] However, a direct proof for the role of *N*-methyleneaniline as an intermediate is now possible for the first time by applying the novel *in situ* SF MAS NMR method. It is obvious that this new NMR technique is an extremely useful tool in heterogeneous catalysis and possesses high potential for elucidating the mechanisms of a broad variety of reactions.

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