AN *IN SITU* ^{13}C MAS NMR STUDY OF THE ZEOLITE-CATALYZED ALKYLATION OF POLAR AROMATICS

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ABSTRACT

In situ ^{13}C MAS NMR was applied to study the mechanisms of the N-alkylation of aniline and of the O-alkylation of phenol with methanol on acidic (H-Y) and basic (CsOH/CsNa-Y) zeolite Y catalysts. Methanol-^{13}C was the labeled reactant. The results point to similar mechanisms of the N- and O-alkylation on Brønsted acid sites including a dehydration of methanol towards dimethyl ether (DME) or surface methoxy groups, which further react with aniline to N-methyalnilinium, N,N-dimethylanilinium, and N,N,N-trimethylanilinium cations or a direct reaction of phenol and methanol towards anisole. At variance, different mechanistic pathways were observed on basic zeolite Y: N-alkylation is shown to proceed via methanol dehydrogenation leading to the formation of formaldehyde species responsible for further methylation, while O-alkylation includes the formation of phenolate ions initiating the alkylation reaction.

Key words: methylation of aniline and phenol, reaction mechanism, ^{13}C MAS NMR spectroscopy, acidic and basic zeolites

INTRODUCTION

Alkylation of polar aromatics on zeolite catalysts has been thoroughly studied during the last two decades. Attention was mainly focused on the application of zeolites in the selective production of valuable alkylated aromatics [1-5]. Mechanistic studies are, however, limited because the reaction patterns on these catalysts are significantly affected by diffusion processes, and the fact that the products observed at the outlet of conventional continuous-flow reactors do not reflect the real situation on the catalyst. Information on the real surface reactions can be obtained by means of recently developed *in situ* spectroscopic techniques. This study aims at the clarification of the mechanisms of the methylation of polar aromatics using *in situ* ^{13}C MAS NMR spectroscopy. Alkylation of aniline and phenol with methanol on acidic and basic zeolites Y were selected as model reactions.

EXPERIMENTAL

Acidic and basic zeolites Y were prepared by ion exchange of zeolite Na-Y with NH_4NO_3 leading to zeolite NH_4-Y and with CsCl followed by impregnation with CsOH leading to zeolite CsOH/CsNa-Y. The ion exchange degrees of NH_4^+ and Cs^+ were 92 and 70 %, respectively. The content of cesium hydroxide in the basic zeolite Y was 14 CsOH per u.c. Methanol-^{13}C (99 % enriched) was purchased from Cambridge Isotope Laboratories, Inc.

The reaction mechanisms were investigated using *in situ* ^{13}C MAS NMR spectroscopy both under batch (BC) and continuous-flow (CF) conditions. ^{13}C BC MAS NMR experiments were carried out on a Bruker MSL300 spectrometer operating at 75.15 MHz using sealed glass inserts fitting precisely into the MAS rotor and containing the catalyst material loaded with the reactants. In a typical NMR experiment, the sealed glass insert was rapidly heated to selected reaction temperature outside the spectrometer and maintained at this temperature for a given period. ^{13}C MAS NMR spectra were recorded at 298 K after quenching the reaction by liquid nitrogen. After recording the NMR spectra, the glass inserts with the catalyst material were returned to reaction temperature and heated for progressively longer periods. A more detailed description of the *in situ* BC MAS NMR experiments is given in References [6] and [7].

In situ ^{13}C CF MAS NMR experiments were performed on a Bruker MSL400 spectrometer at a resonance frequency of 100.6 MHz. Prior to the *in situ* CF MAS NMR experiments, the calcined zeolite materials were filled into a 7 mm MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the high-temperature Doty MAS NMR probe, a second *in situ* dehydration of the catalyst material was performed at 673 K for 1 h under flowing nitrogen (30 ml/min). During the *in situ* MAS NMR experiments under continuous-flow conditions at temperatures between 298 and 523 K, carrier gas (dry nitrogen) loaded with $^{13}CH_3OH$ and aniline or phenol was injected into the MAS NMR rotor reactor applying the equipment described elsewhere [8]. In different experiments, modified residence times, *W*/*F*, of $^{13}CH_3OH$ between 20 and 100 g·h/mol were used, and the molar $^{13}CH_3OH$ to aniline and $^{13}CH_3OH$ to phenol ratios were varied from 1 : 1 to 4 : 1. A more detailed description of the CF MAS NMR experiments is given in References [9] and [10].

RESULTS AND DISCUSSION

Methylation of aniline and phenol on acidic zeolite H-Y

Figures 1 and 2 show ^{13}C MAS NMR spectra recorded under batch conditions after adsorption and reaction of methanol-^{13}C with aniline and phenol, respectively, on zeolite H-Y. Co-adsorption of methanol-^{13}C and aniline on zeolite H-Y at ambient temperature resulted in the occurrence of three ^{13}C MAS NMR signals due to labeled methanol species with different mobility (Fig. 1): mobile "intracrystalline" methanol (49 ppm), species with limited mobility due to an interaction of the methanol with strongly adsorbed aniline molecules (51 ppm) and small amounts of strongly bound surface methoxy groups (56 ppm). The above signal assignments were discussed in detail previously [6].

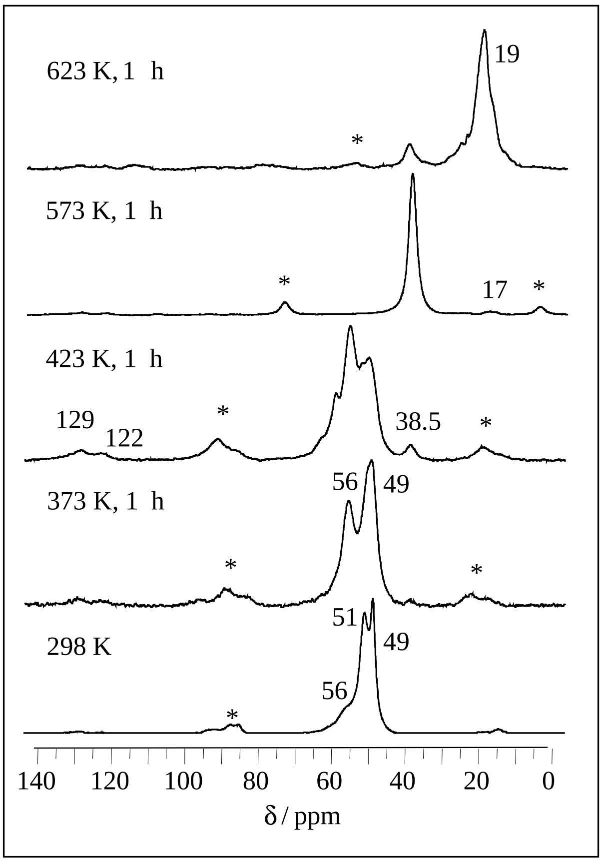

Figure 1: ^{13}C MAS NMR spectra recorded under batch conditions in the course of the reaction of aniline (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite H-Y. Asterisks indicate spinning sidebands [6].

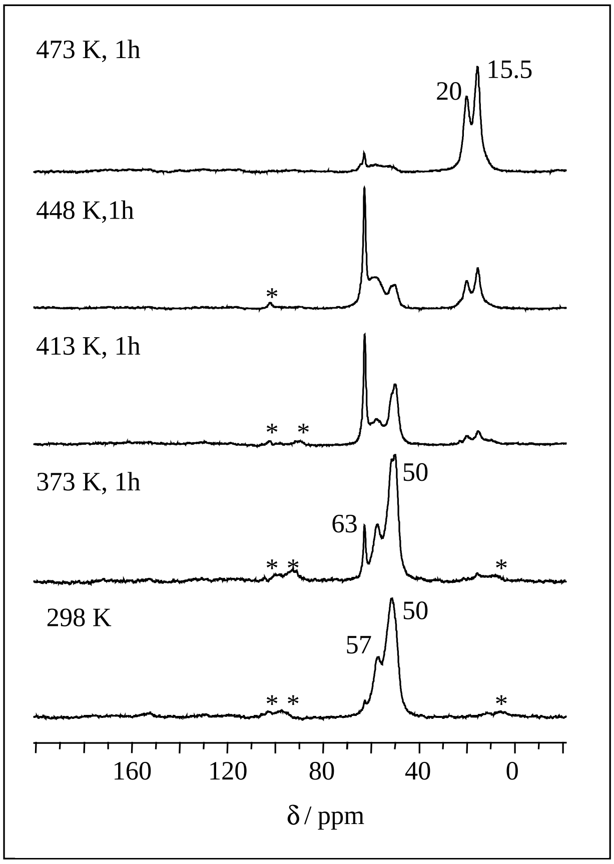

Figure 2: ^{13}C MAS NMR spectra recorded under batch conditions in the course of the reaction of phenol (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite H-Y. Asterisks indicate spinning sidebands.

In the case of the reaction of phenol and methanol, three ^{13}C MAS NMR signals were identified (Fig. 2): Strongly adsorbed methanol (50 ppm) and two new signals at ca. 57 and 63 ppm. The line at 57 ppm was attributed to the methyl group of anisole. This assignment was confirmed by adsorption of pure anisole on zeolite H-Y. The 2 ppm shift of this signal with respect to solution data (54.8 ppm [11]) is due to an interaction of anisole with Brønsted acid sites, leading to significant disturbance of its methyl group. The line at 62 to 63 ppm was previously attributed to side-on adsorption species of dimethyl ether (DME) [12]. This assignment, however, does not seem appropriate in our case due to the following reasons:

- DME is usually formed from methanol on zeolite catalysts at reaction temperatures higher than 373 K. In our case, the line at 63 ppm is observed already at ambient temperature.
- Formation of DME side-on adsorbed species is usually accompanied by occurrence of end-on adsorbed species, which are not observed in our case.
- The line corresponding to side-on adsorbed species of DME is usually broad and amenable to cross-polarization, which is not the case in our experiments.

At present, we do not have unambiguous experimental proofs for the assignment of the resonance line observed at 63 ppm. One possibility is that it is due to protonated anisole. Further experiments are in progress to verify this hypothesis.

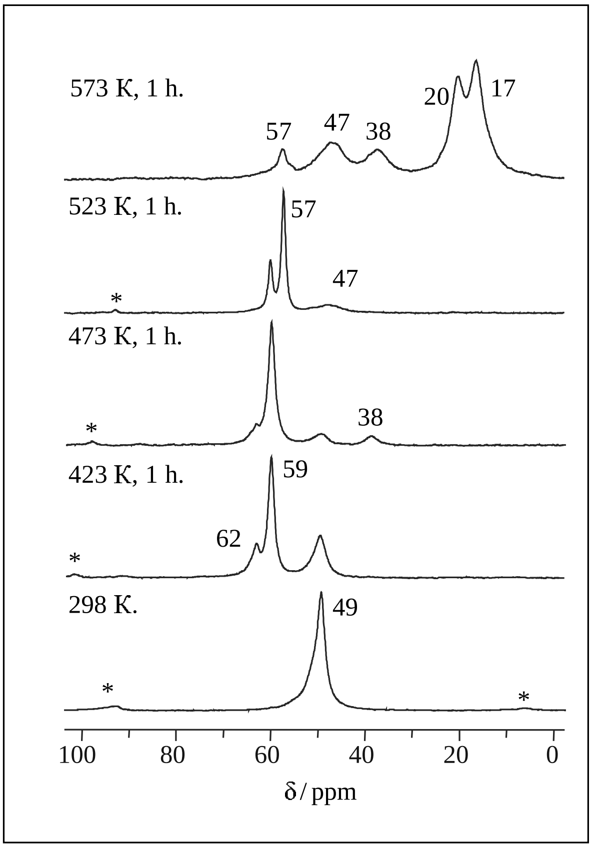

Figure 3: ^{13}C MAS NMR spectra recorded under batch conditions in the course of the reaction of aniline (10 molecules/u.c.) and methanol-^{13}C (40 molecules/u.c.) on zeolite H-Y. Asterisks indicate spinning sidebands.

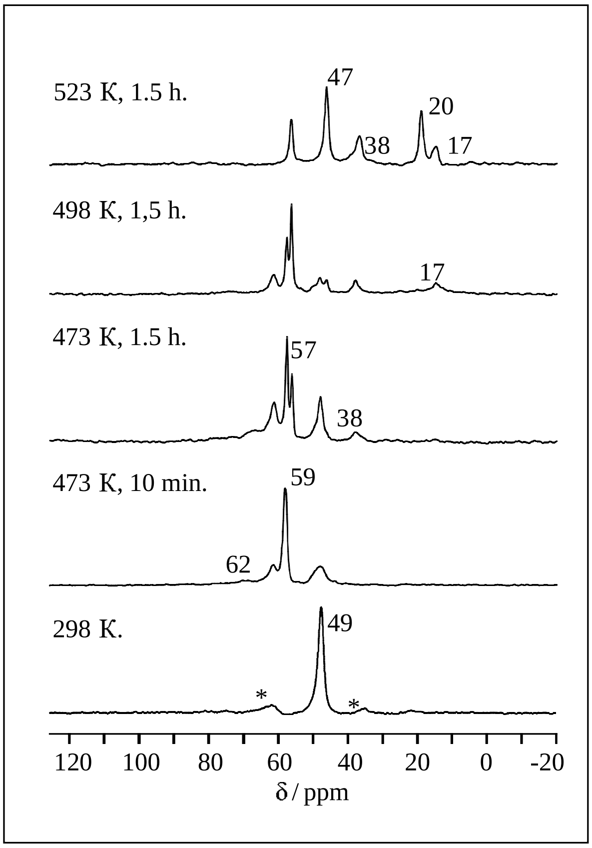

Figure 4: ^{13}C MAS NMR spectra recorded under continuous-flow conditions in the course of the reaction of aniline and methanol-^{13}C on zeolite H-Y (*W/F* = 40 g·h/mol, methanol/aniline = 2 : 1). Asterisks indicate spinning sidebands [9].

The reaction observed after heating zeolite H-Y loaded with methanol and aniline led to a conversion of methanol to surface methoxy species and a small amount of DME (Fig. 1). The latter compound was evidenced by two ^{13}C MAS NMR signals at ca. 59 and 62 ppm, corresponding to end-on and side-on adsorbed species of dimethyl ether. Methoxy species and DME were further converted to N-methylanilinium cations, confirmed by the resonance at 38.5 ppm [6,7]. At a reaction temperature of 573 K, a complete conversion of all ^{13}C-labeled species to methyl groups of N-methylaniline was observed, suggesting that N-methylaniline is the only primary alkylation product on zeolite H-Y. The formation of secondary reaction products, such as toluidines and N-methyltoluidines, evidenced by the appearance of ^{13}C MAS NMR signals at 17 to ca. 19 ppm, was observed only at reaction temperatures of $T \geq 573$ K after complete conversion of methanol species into N-methylaniline (Fig. 1).

Heating of phenol and methanol on zeolite H-Y at temperatures of 298 to 413 K resulted in a gradual conversion of methanol and phenol to anisole (Fig. 2). At higher temperatures, the latter species were further converted into cresols as confirmed by the appearance of signals at 15.5 to 20 ppm.

When the reaction was carried out at a higher loading with the reactants or under continuous-flow conditions, additional features were observed in the case of the interaction of methanol with aniline (Figs. 3 and 4):

- Instead of methoxy groups, large quantities of DME were observed upon methanol dehydration.
- Besides N-methylanilinium (38 ppm) cations, also N,N-dimethylanilinium (47 ppm) and N,N,N-trimethylanilinium (57 ppm) cations were observed as the products of the N-methylation.

In the case of a conversion of phenol and methanol at higher loadings, DME was also observed in larger amounts, however, no other products of alkylation were detected.

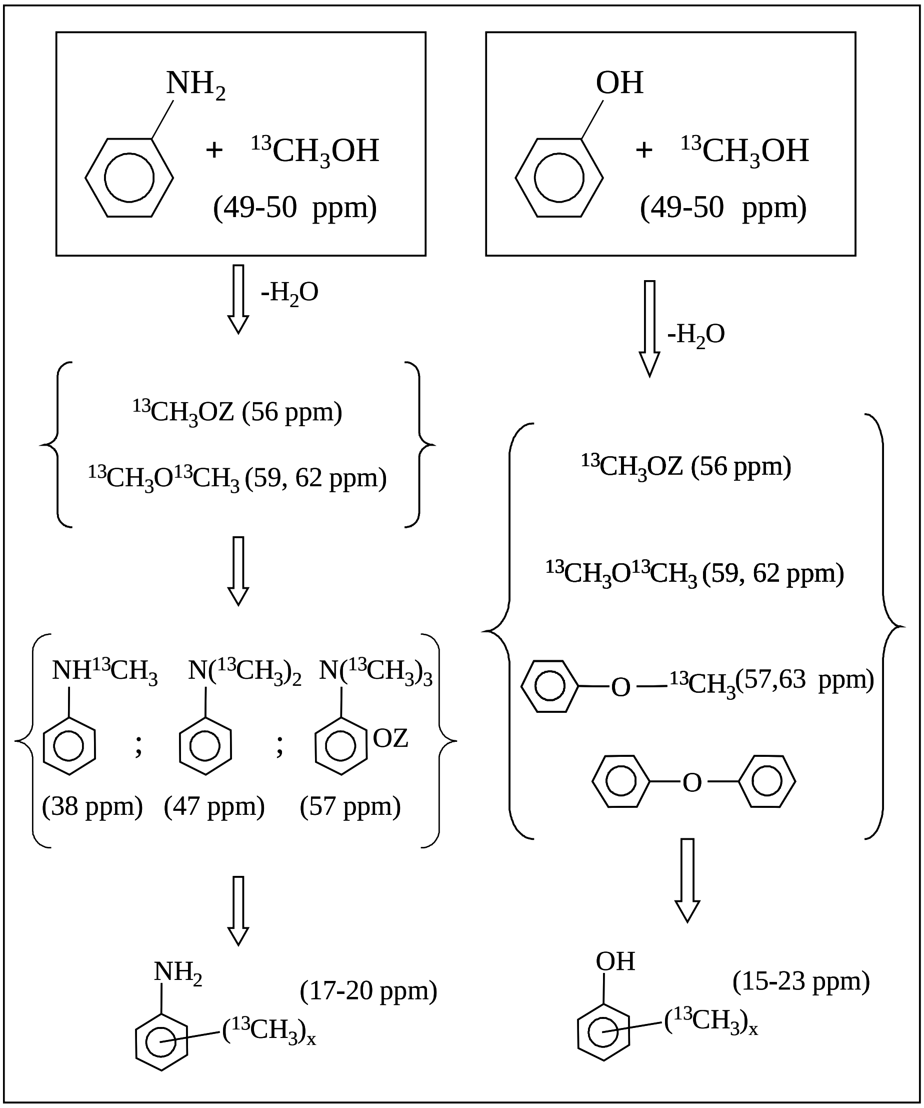

Figure 5: Mechanistic pathways of aniline and phenol methylation on zeolite H-Y.

The mechanistic pathways for the methylation of aniline and phenol on zeolite H-Y presented in Figure 5 rationalize the above-mentioned observations. In both methylation reactions, the first reaction step is a dehydration. The reaction of methanol and aniline includes a dehydration of methanol to surface methoxy groups or a conversion to DME, which further react with aniline to N-methyalnilinium, N,N-dimethylanilinium, and N,N,N-trimethylanilinium cations. The dehydration of methanol in the presence of phenol results in a direct formation of anisole. At elevated temperatures, methylanilinium cations and anisole are converted via a secondary isomerization reaction to toluidines or cresols, respectively.

Methylation of aniline and phenol on basic zeolite CsOH/CsNa-Y

^{13}C MAS NMR spectra observed upon adsorption and reaction of methanol with aniline or phenol on zeolite CsOH/CsNa-Y under batch conditions and at low loadings of the reactants are presented in Figures 6 and 7, respectively. In contrast to acidic zeolite H-Y, only one type of methanol species at 49 to 50 ppm was observed on the basic zeolite Y at ambient temperature. The significant line broadening, the appearance of spinning sidebands and the enhancement of the signal intensity by application of the cross-polarization technique suggest that the signal at 49 to 50 ppm corresponds to strongly adsorbed methanol.

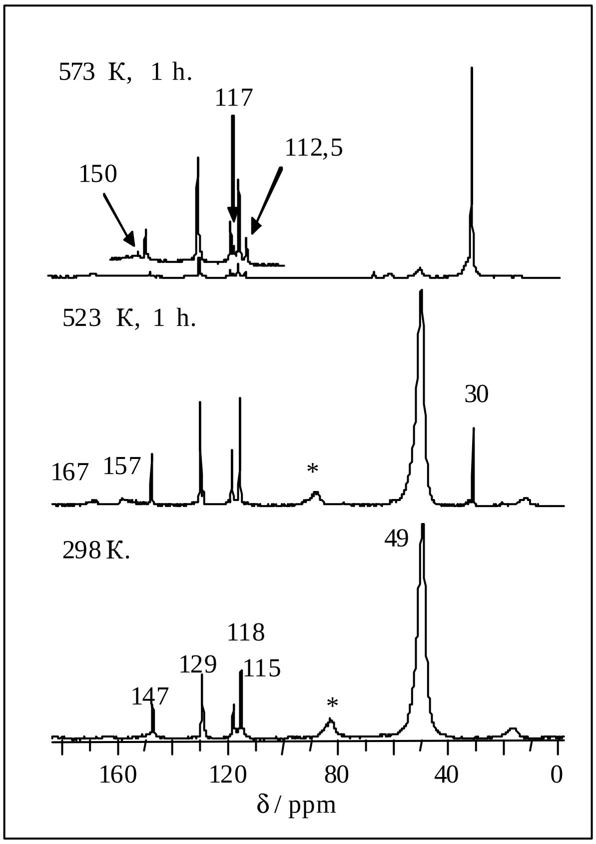

Figure 6: ^{13}C MAS NMR spectra recorded under batch conditions in the course of the reaction of aniline (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite CsOH/CsNa-Y. Asterisks indicate spinning sidebands.

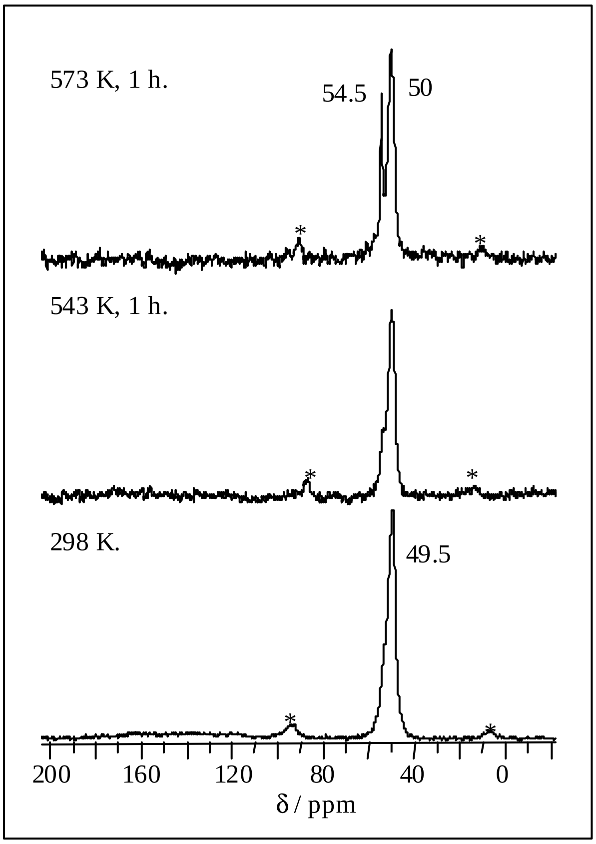

Figure 7: ^{13}C MAS NMR spectra recorded under batch conditions in the course of the reaction of phenol (21 molecules/u.c.) and methanol-^{13}C (7 molecules/u.c.) on zeolite CsOH/CsNa-Y. Asterisks indicate spinning sidebands.

As evidenced by the observation of the signals at 30 ppm due to the labeled methyl group of N-methylaniline (Fig. 6) and at 54.5 ppm due to the labeled methyl group of anisole (Fig. 7), the alkylation reactions start in the temperature range of 523 to 543 K. It is important to note that, in the case of zeolite CsOH/CsNa-Y, the interpretation of the signals corresponding to N-methylaniline and anisole is straightforward since the chemical shifts are close to the solution data (29.9 and 54.4 ppm, respectively [11]). Heating of the catalyst at higher temperatures resulted in a further methylation of aniline and phenol. The reaction was faster in the case of aniline: at 573 K, practically all methanol molecules were converted leading to N-methylaniline (Fig. 6), while less than 30% of the methanol molecules reacted with phenol at the same reaction temperature (Fig. 7).

In the case of the reaction of aniline with methanol, two broad ^{13}C MAS NMR signals occurred at ca. 167 and 157 ppm at the onset of the N-methylaniline formation (Fig. 6). These lines were much better observed under continuous-flow conditions, as shown in Figure 8. The line at 167 ppm is assigned to surface formate species, while the line at 157 ppm is attributed to N-methyleneaniline [10]. The observation of N-methyleneaniline as an intermediate species suggests that on basic zeolite Y, methylation of aniline proceeds via methanol dehydrogenation to formaldehyde, condensation of aniline with formaldehyde to N-methyleneaniline and hydrogenation of N-methyleneaniline to N-methylaniline by H_2 produced during the first reaction step (Fig. 9).

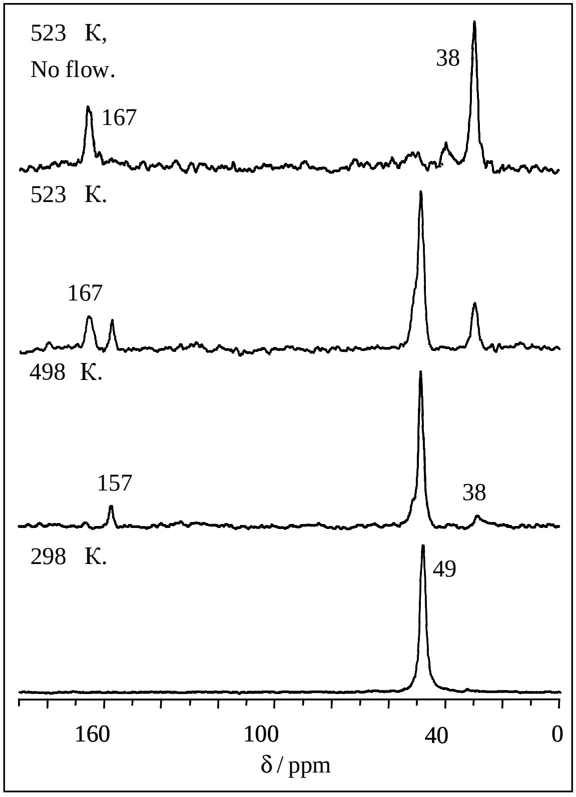

Figure 8: ^{13}C MAS NMR spectra recorded under continuous-flow conditions in the course of the reaction of aniline and methanol-^{13}C on zeolite CsOH/CsNa-Y (*W/F* = 40 g·h/mol, molar methanol/aniline ratio of 4 : 1) [10].

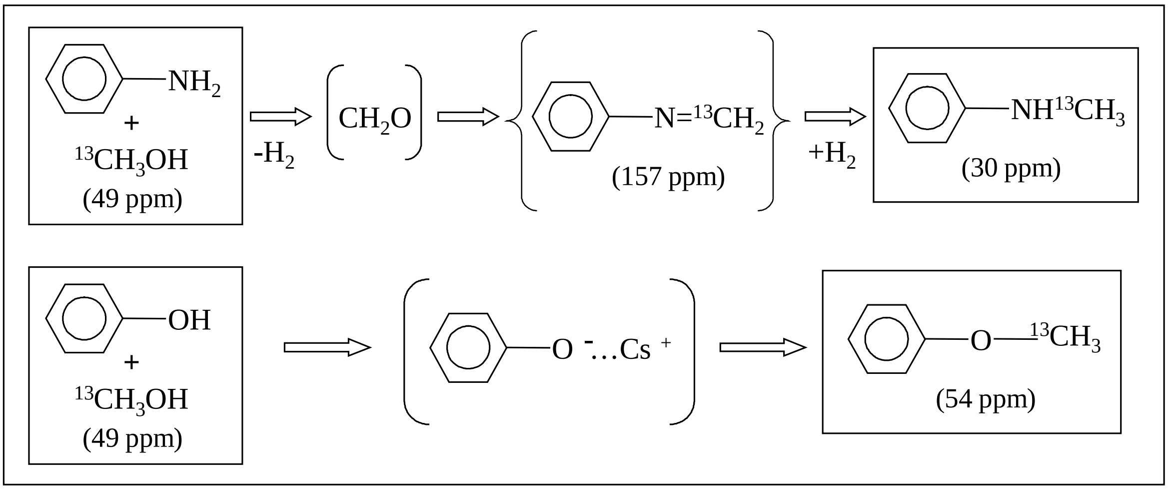

Figure 9: Mechanistic pathways of aniline and phenol methylation on basic zeolite CsOH/CsNa-Y.

It is obvious that the mechanism proposed for the methylation of aniline cannot be extended to the methylation of phenol, since formaldehyde does not react with phenol in a similar way. The present ^{13}C MAS NMR experiments have not revealed any intermediates in the course of the latter reaction on zeolite CsOH/CsNa-Y. The data obtained by *in situ* FTIR spectroscopy [13] pointed to an intermediate formation of phenolate species, evidenced by the appearance of IR bands at 1312 cm^{-1} and 1579 cm^{-1} in the course of the methylation of phenol on the same catalyst. Based on these results, we propose that the O-methylation on zeolite CsOH/CsNa-Y proceeds via formation of phenolate species on cesium sites. These species further react with methanol to anisole as shown in Figure 9. It should be mentioned that the phenolate species could not be observed by ^{13}C MAS NMR spectroscopy, since in the present experiments phenol was not labeled. Additional experiments with phenol-1-^{13}C as labeled reactant are in progress to support the mechanism proposed for the methylation of phenol.

CONCLUSIONS

In situ ^{13}C MAS NMR investigations have demonstrated that the first reaction step of the methylation of aniline and phenol by methanol on acidic zeolite Y is a dehydration reaction. The reaction of methanol and aniline includes the dehydration of methanol to surface methoxy groups and dimethyl ether, which further react with aniline to N-methylanilinium, N,N-dimethylanilinium, and N,N,N-trimethylanilinium cations. At variance, the reaction of methanol and phenol results in the direct formation of anisole occurring already at ambient temperature. At elevated temperatures, methylanilinium cations and anisole are converted into toluidines and cresols, respectively, via secondary isomerization reactions.

On basic zeolite Y, anisole is formed via a reaction of methanol with phenolate species on cesium sites. N-alkylation proceeds via a more complicated reaction pathway including methanol dehydrogenation to formaldehyde species, alkylation of aniline with formaldehyde to N-methyleneaniline, and hydrogenation of N-methyleneaniline to N-methylaniline.

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