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Surface Species Formed during Aniline Methylation on Zeolite H–Y Investigated by *in Situ* MAS NMR Spectroscopy

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Aniline alkylation with methanol on zeolite H–Y has been studied using *in situ* ^{13}C MAS NMR spectroscopy under batch conditions. To clarify the main reaction pathways, the conversion of methanol as well as the interaction of aniline with surface methoxy groups were investigated under similar conditions. Methanol-^{13}C and methyl iodide-^{13}C were used as labeled reactants. Co -adsorption of aniline and methanol-^{13}C on zeolite H–Y led to strongly adsorbed aniline molecules, assigned to aniline H-bonded to zeolite Brønsted acid sites, and three types of methanol species of different mobility: mobile methanol molecules with a liquid-like characteristics and two types of rigid methanol species with solid-like characteristics attributed to a methanol adsorption complex with aniline and surface methoxy groups, respectively. Among all the methanol species observed, only surface methoxy groups were shown to be responsible for aniline alkylation which takes place at temperatures from 373 to 523 K. The formation of surface methoxy groups was found to be a limiting step of the overall reaction. The primary alkylation product is *N*-methylaniline. Toluidines and *N*-methyltoluidines are formed at temperatures from 523 to 623 K after complete conversion of methanol to *N*-methylaniline. Therefore, isomerization or disproportionation of *N*-methylaniline was proposed to account for their formation.

INTRODUCTION

Methylation of aniline is an industrially important process, aimed at the synthesis of mono-*N*-methylaniline, di-*N*-methylaniline, and toluidine, which are useful raw materials for organic syntheses as well as important intermediates in the dye-stuff production and in the pharmaceutical and agrochemical industries. Until now, industrial processes leading to these products are based on the application of corrosive liquid acids as catalysts (1, 2) and should be replaced by environmentally more benign processes using solid catalysts such as oxides, clays, and zeolites (3–8). However, the formation of the target alkylation products on these catalysts is often accompanied by the formation of by-products such as various C-alkylated anilines and polymers leading to catalyst deactivation (6–8). It is known that alkylation of aniline may take place on acidic (3–6) and on basic zeolites (7, 8). Moreover, this reaction was performed even on zeolites with redox properties (3, 9, 10). A detailed understanding of the mechanisms of the main and side reactions occurring during alkylation on various types of zeolites and the determination of the active sites and their role in each elementary step may give a key to the design of new solid catalysts with the required properties. Such mechanistic information can be obtained by recently developed *in situ* MAS NMR spectroscopic technique (11–19). Among these studies, the investigations on the interaction of methanol with ammonia over mordenite (20) and H–RHO and H–SAPO-34 (21) catalysts are the closest to the above subject. However, according to our knowledge, no direct data are available as yet on the mechanism of aniline methylation on zeolites.

This study aims at a clarification of the mechanism of aniline methylation over acidic zeolite Y. *Controlled-atmosphere* ^{13}C MAS NMR spectroscopy under batch conditions using samples sealed in glass cells was employed for this purpose. The attention is focused on the following:

1. identification of the reaction intermediates which may play a role as alkylating agents;
2. determination of the primary and secondary reaction products;
3. investigation of the mechanisms leading to C- and N-alkylation.

EXPERIMENTAL

Materials

Zeolite Na–Y with an $n_{\mathrm{Si}}/n_{\mathrm{Al}}$ ratio of 2.6 was obtained from Union Carbide (Tarrytown, NY). The H$^+$ form of the zeolite (H–Y) was prepared by fourfold ion exchange in an 1 M aqueous solution of NH_4NO_3 and subsequent calcination at 673 K (*vide infra*). The material was characterized using XRD, electron microscopy, atomic emission spectroscopy with inductively coupled plasma (AES-ICP),

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FTIR, solid state ^1H, ^{27}Al and ^{29}Si MAS NMR spectroscopy, nitrogen adsorption, and temperature-programmed desorption of ammonia. ^{27}Al and ^{29}Si MAS NMR indicated that no dealumination occurred and that the Si/Al ratio in the zeolite framework is close to those determined by chemical analysis. ^1H MAS NMR spectrum corresponded to the spectrum of an intact H–Y zeolite (18).

The labeled reactants methanol-^{13}C (99.9% enriched) and methyl iodide-^{13}C (99.9% enriched) were purchased from ICON Services Inc. and Sigma–Aldrich, respectively. Aniline was obtained from Promochem.

Controlled-Atmosphere ^{13}C MAS NMR Measurements

Controlled-atmosphere *in situ* NMR experiments were performed in sealed glass cells containing the loaded catalyst and an adsorbate and fitting precisely into 7-mm Bruker MAS NMR rotors. The powdered catalyst samples (0.08 ± 0.01 g) were packed into the NMR tubes (Wilmad, 5.6-mm o.d. with constrictions), evacuated to a final pressure of 10^{-3} Pa after heating for 12 h at 673 K, and cooled down to 298 K before the adsorption of reactants. In different experiments, the catalyst samples were loaded with methanol-^{13}C, aniline, or mixtures of aniline and methanol-^{13}C (Table 1). For some experiments, the zeolite samples were methoxylated prior to aniline adsorption by treatment with ^{13}C-labeled CH_3OH or CH_3I at 433 K for 5 h. The treated samples were then evacuated at 393 K to remove unreacted methoxylating agents. After adsorption of all reactants, the NMR cells, maintained at 77 K to ensure a quantitative adsorption, were carefully sealed to achieve proper rotor balance and high spinning rates in the MAS NMR probe.

^{13}C MAS NMR measurements were carried out on an MSL-300 Bruker spectrometer operating at 75.15 MHz. Conditions allowing a quantitative evaluation were achieved using high-power gated proton decoupling with suppressed nuclear Overhauser effect. Experiments with cross-polarization (contact time 3 ms) were performed to distinguish between species of different mobilities. Repetition times of 5 s were used both for the MAS and CP/MAS NMR measurements. For each spectrum, between 400 and 8000 free induction decays were accumulated with a sample spinning rate of 3.0–3.5 kHz.

TABLE 1

Catalyst Samples Prepared in Sealed Glass Cells for the Controlled-Atmosphere ^{13}C MAS NMR Investigations under Batch Conditions

Catalyst	Loaded reactants (in molecules/u.c.)		
	Methanol-^{13}C	Methyl iodide-^{13}C	Aniline
H–Y	—	—	21
H–Y	7	—	—
H–Y	7	—	21
H–Y	—	15	—
H–Y, methoxylated by CH_3OH-^{13}C	—	—	21
H–Y, methoxylated by CH_3I-^{13}C	—	—	10

In a typical NMR experiment, the sealed sample cell was rapidly heated to the selected temperature outside the spectrometer and maintained at this temperature for a given period of time. MAS NMR spectra were recorded at 293 K after the sample cell was quenched in liquid nitrogen. After the NMR data were collected, the sample cell was returned to reaction conditions. The experimental temperature was increased stepwise, and spectra were recorded as a function of temperature.

RESULTS AND DISCUSSION

1. *Adsorption of the Reactants Methanol and Aniline*

Figure 1 shows *in situ* ^{13}C MAS NMR and ^{13}C CP/MAS NMR spectra observed after adsorption of aniline, methanol-^{13}C, and an aniline–methanol-^{13}C mixture on zeolite H–Y. Adsorption of aniline leads to a broad sideband pattern with ^{13}C MAS NMR central lines at ca. 122 and 129 ppm. The occurrence of the broad sideband pattern indicates that the aniline molecules are rigidly bound to the zeolite framework. The signal at ca. 129 ppm corresponds to aniline carbon atoms in meta positions and is very close to the corresponding value in solution (129.1 ppm (22)). In contrast, the signal at ca. 122 ppm assigned to carbon atoms in ortho and para positions is shifted significantly to lower field (solution data: 114.4 and 116.3 ppm, respectively (22)). This result suggests that, upon aniline adsorption, Brønsted acid sites of zeolite H–Y interact with the NH_2 groups of aniline molecules, causing a significant distortion of the carbon atoms in ortho and para positions and points to a partial protonation of the aniline molecules adsorbed on zeolite H–Y.

The ^{13}C MAS NMR spectrum observed after adsorption of methanol-^{13}C shows two resonances: a broad and weak signal at ca. 56 ppm and a narrow intense line at ca. 49 ppm. The narrow line at 49 ppm with liquid-like characteristics is attributed to mobile methanol species, which are most probably attached to bridging hydroxyls, as was shown in (23). The broad signal at 56 ppm corresponding to more rigid species, which are amenable to cross-polarization, is assigned to surface methoxy groups. The chemical shift and the behavior of the latter species are consistent with previous observations for surface methoxy groups obtained by reaction with methyl iodide over zeolite H–Y (24, 25).

Co-adsorption of aniline and methanol-^{13}C results in the appearance of a new resonance line at ca. 51 ppm

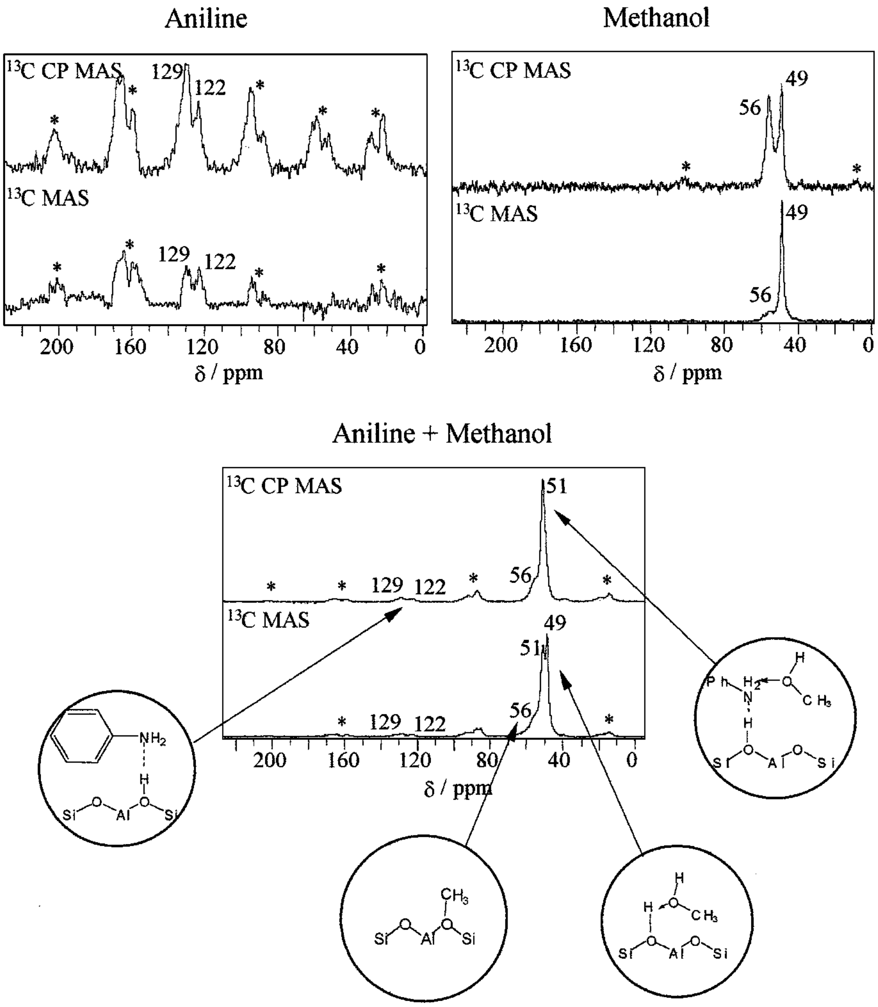

FIG. 1. ^{13}C MAS NMR and ^{13}C CP/MAS NMR spectra recorded after adsorption of aniline, methanol-^{13}C, and a mixture of methanol-^{13}C and aniline on zeolite H–Y at 293 K. Asterisks indicate spinning sidebands.

corresponding to rigid species as evidenced by the experiment with cross-polarization. This line could be caused by methanol interacting with aniline, which is H-bonded to Brønsted acid sites of zeolite H–Y (aniline/methanol adsorption complex).

To conclude, the results of NMR spectroscopy give the following picture of aniline and methanol adsorption on zeolite H–Y. Aniline, which is more strongly adsorbed than methanol, is supposed to be H-bonded to Brønsted acid sites of zeolite H–Y. As a result, positive charge is partially transferred to the NH_2 group of the aniline molecule, leading to the formation of a surface aniline complex. A small part of the methanol molecules (ca. 15%) also interacts with Brønsted acid sites of the zeolite to form surface methoxy groups; another part (ca. 55%) gives adsorption complexes with H-bonded aniline molecules and the remainder (ca. 30%) is present as methanol molecules with high mobility.

2. Aniline Alkylation with Methanol

^{13}C MAS NMR spectra recorded after reaction of aniline with methanol on zeolite H–Y are presented in Fig. 2. Alkylation of aniline starts at 373 K, as evidenced by the appearance of a small signal at 38.5 ppm attributed to the methyl groups of *N*-methylaniline. This assignment was confirmed by adsorption of pure *N*-methylaniline on zeolite H–Y. The significant shift of the line corresponding to *N*-methylaniline with respect to solution data (29.9 ppm (22)) is due to a strong interaction between the basic–NH–groups of the *N*-methylaniline molecules and zeolite Brønsted acid sites, leading to a significant disturbance of the methyl groups. The appearence of a new NMR signal at 38.5 ppm is accompanied by the increase of the concentration of methoxy species from 15% up to 45% and by merging of the lines at 49 and 51 ppm into a very broad signal centered at ca. 49 ppm. This merger is due to the

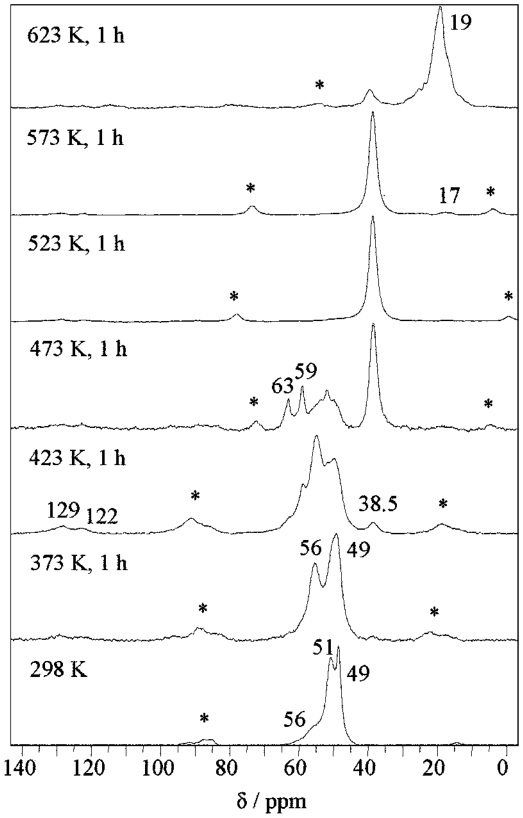

FIG. 2. ^{13}C MAS NMR spectra recorded in the course of reaction between methanol-^{13}C and aniline on zeolite H–Y. Asterisks indicate spinning sidebands.

decrease of the contribution of the line at 51 ppm caused by a destruction of a part of the aniline adsorption complexes and removal of the corresponding aniline molecules from Brønsted acid sites into the gas phase by the more stable surface methoxy groups.

At a temperature of 423 K, the line at 56 ppm corresponding to surface methoxy groups yields the highest contribution to the NMR spectrum. The concentration of *N*-methylaniline at 38.5 ppm also increases. In addition, two small resonance lines at ca. 59 and 63 ppm appear, which are due to different forms of adsorbed dimethyl ether (26).

Further heating to 473 K leads to a disappearance of the signal of surface methoxy groups followed by a rapid formation of *N*-methylaniline. This observation suggests that methoxy groups may play a role as intermediates in the *N*-alkylation on zeolite H–Y.

Finally, at a temperature of 523 K, all ^{13}C-labeled species are converted into methyl groups of *N*-methylaniline molecules. Consequently, *N*-methylaniline is the only primary alkylation product on zeolite H–Y, and surface methoxy groups are suggested to be intermediates in this reaction.

Formation of the secondary reaction products, viz. toluidines and *N*-methyltoluidines, evidenced by the appearance of ^{13}C NMR signals at 17 to 24 ppm (Fig. 2), is observed only at reaction temperatures from 523 to 623 K after complete conversion of methanol species into *N*-methylaniline. It is hence concluded that toluidines and *N*-methyltoluidines are formed via isomerization or disproportionation of *N*-methylaniline.

3. *Interaction of Aniline with Methoxylated Zeolite H–Y*

To confirm the intermediate role of surface methoxy groups in aniline alkylation with methanol, the methoxylation of zeolite H–Y with methanol and methyl iodide and the interaction of aniline with the methoxylated zeolite were studied. The corresponding ^{13}C MAS NMR spectra are presented in Figs. 3 and 4.

As discussed in section 1, adsorption of methanol on evacuated zeolite H–Y leads to the formation of surface methoxy groups already at ambient temperature. However, the concentration of methoxy groups at this temperature is rather low. Therefore, the sample with adsorbed methanol was heated in a stepwise manner to find the optimal temperature for the formation of methoxy groups (Fig. 3a). The spectra show that the maximum intensity of the signal due to methoxy groups occurs at 438 K. Further heating leads to the formation of dimethyl ether (59 ppm) and finally results in the conversion of methanol to hydrocarbons evidenced by the appearance of a large number of lines in the spectral region between 0 and 35 ppm.

The ^{13}C MAS NMR spectra obtained after methoxylation of zeolite H–Y with methyl iodide are shown in Fig. 3b. With this reactant, the reaction is much more difficult and only a small part of CH_3I is converted to surface methoxy groups, even at elevated temperatures. The optimal temperature of methoxylation with CH_3I is around 430 to 450 K, as in the case of methoxylation by methanol. At higher temperatures, the methoxy groups are converted into hydrocarbons. The possibility to remove unreacted methyl iodide was checked in a separate experiment in which the sample loaded with methyl iodide was first heated to 433 K for 5 h and then evacuated at 393 K. The spectrum presented in Fig. 3b, top, shows a partial surface methoxylation (signal at 56 ppm) and satisfactory removal of the unreacted reagent (signal at −23 ppm). Therefore, the latter conditions were selected for a methoxylation of the zeolite surface with both methanol and methyl iodide.

After methoxylation, the samples were further subjected to aniline adsorption at ambient temperature. It is interesting to note that *N*-alkylation, evidenced by the appearance of the line at 38.5 ppm, is observed already at this temperature (Fig. 4). Further heating at temperatures from 373 to 473 K leads to a complete transformation of the surface methoxy groups into *N*-methylaniline. It should be mentioned that, in the case of zeolite H–Y methoxylated with methanol, the reaction with aniline is slower since the evacuation procedure did not allow removal of all unreacted methanol and water formed during methoxylation.

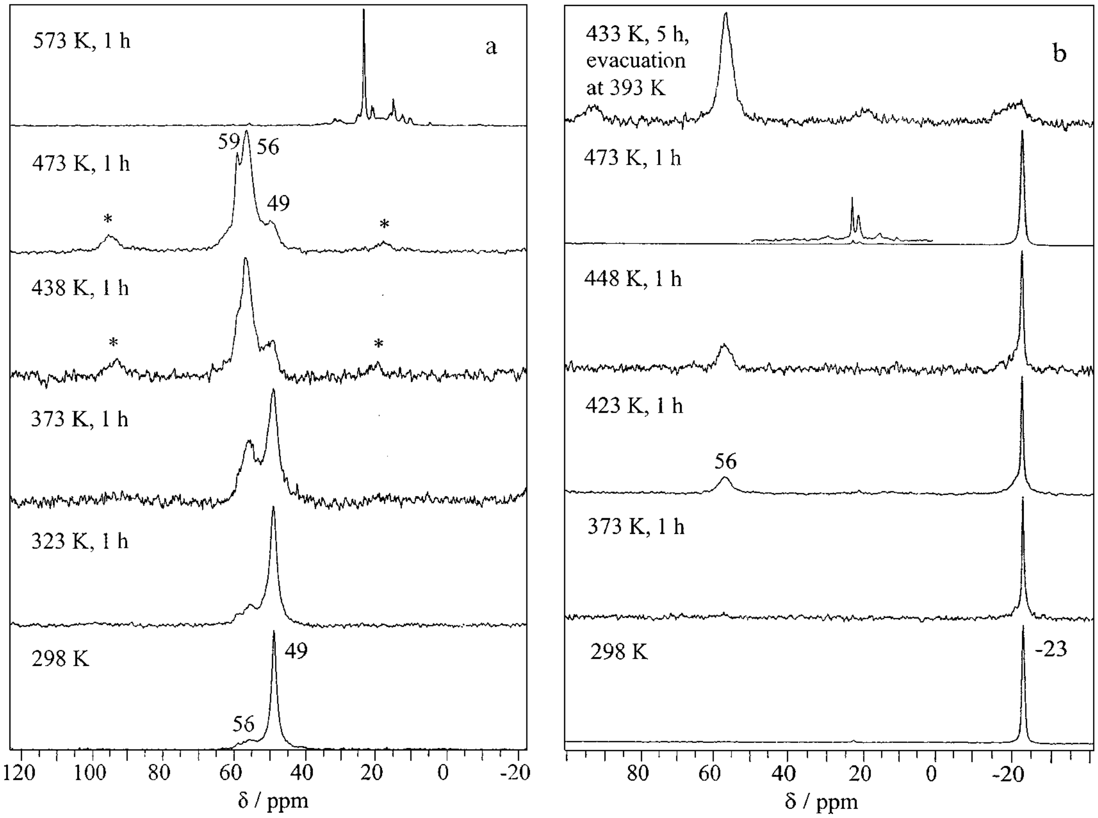

FIG. 3. ^{13}C MAS NMR spectra recorded during reactions of methanol-^{13}C (a) and methyl iodide-^{13}C (b) on zeolite H–Y. Asterisks indicate spinning sidebands.

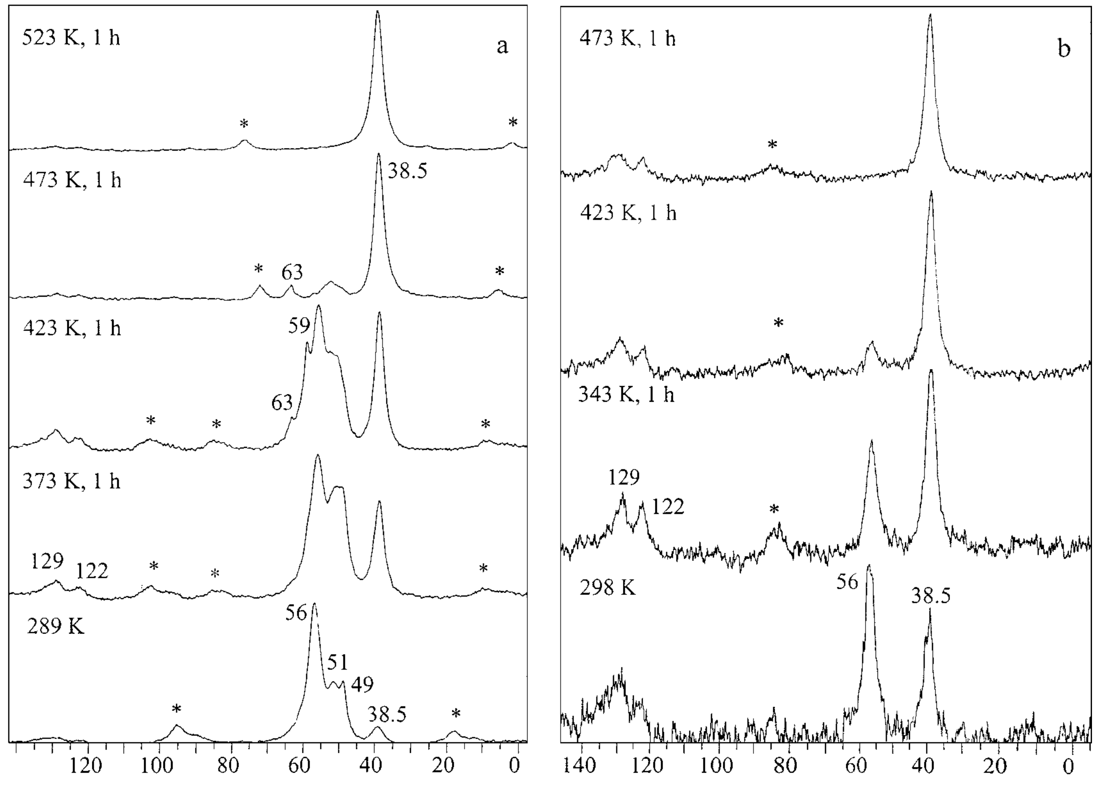

FIG. 4. ^{13}C MAS NMR spectra recorded during reaction of aniline on zeolite H–Y methoxylated by methanol-^{13}C (a) and methyl iodide-^{13}C (b). Zeolite methoxylation was carried out prior to aniline adsoprtion by treatment with ^{13}C labeled CH_3OH (a) or CH_3I (b) at 433 K for 5 h followed by evacuation at 393 K to remove unreacted methoxylating agent. Asterisks indicate spinning sidebands.

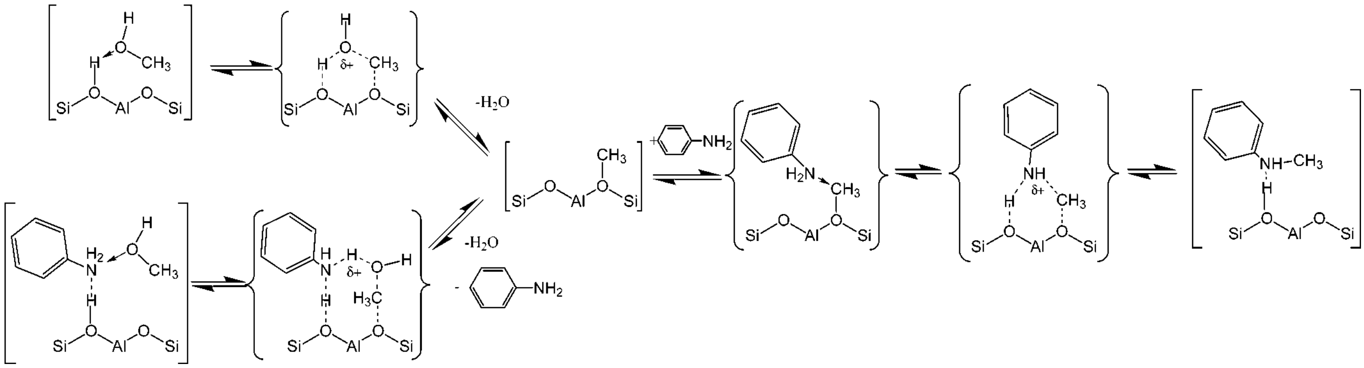

FIG. 5. Mechanism proposed for aniline alkylation with methanol on zeolite H–Y.

In conclusion, the results obtained confirm the hypothesis on the intermediate role of methoxy species in *N*-alkylation. Moreover, the *in situ* ^{13}C MAS NMR investigations demonstrated that the formation of methoxy species is the limiting step of the overall reaction.

4. *Mechanism of the Methylation of Aniline by Methanol*

The reaction mechanism proposed in Fig. 5 rationalizes the experimental results described in sections 1 to 3.

Upon adsorption, the aniline molecules are H-bonded to the Brønsted acid sites of zeolite H–Y and occupy most of these sites. A small part of methanol molecules reacts with free Brønsted acid sites to form surface methoxy groups. Another part gives adsorbate complexes with H-bonded aniline molecules, and the remainder is present as methanol molecules with high mobility.

In the first step, methanol reacts with the zeolite surface to give methoxy groups. This reaction may occur via two reaction pathways, namely, a direct interaction of methanol with free Brønsted acid sites or an interaction of methanol with H-bonded aniline molecules. The first reaction pathway was thoroughly investigated by quantum chemical calculations (27, 28) and was suggested to proceed via a methoxonium-like ion-pair complex (six-membered transition state). The second pathway may occur via a similar mechanism including an eight-membered transition state (Fig. 5). As a result of this step, a part of the aniline molecules is displaced from the Brønsted acid sites into the gas phase by the more stable surface methoxy groups.

In the second step of the reaction, aniline molecules react with surface methoxy groups to give *N*-methylaniline. The latter reaction may occur via a concerted mechanism involving a six-membered transition state, as shown in the right part of Fig. 5.

The experimental data suggest that the second reaction step is much faster than the first one and that the formation of surface methoxy groups is the limiting step of the overall reaction.

CONCLUSIONS

Co-adsorption of aniline and methanol on zeolite H–Y leads to strongly adsorbed aniline molecules and three types of methanol species with different mobility: (i) mobile methanol molecules adsorbed on bridging hydroxyls, (ii) methanol molecules with limited mobility due to an interaction with H-bonded aniline, and (iii) a small amount of methoxy groups strongly bound to the zeolite surface.

N-Methylaniline is the primary product of aniline alkylation. Surface methoxy groups play a role of intermediate species in *N*-alkylation. The limiting step of the reaction is the formation of surface methoxy groups.

Formation of toluidines and *N*-methyltoluidines occurs via secondary isomerization or disproportionation of *N*-methylaniline.

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