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CATALYTIC REACTION MECHANISMS

Mechanism of Aniline Methylation on Zeolite Catalysts Investigated by *In Situ* ^{13}C NMR Spectroscopy

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Abstract—The alkylation reaction of aniline with methanol on zeolites HY and CsOH/CsNaY was studied by *in situ* ^{13}C NMR spectroscopy under flow and batch conditions. Attention was focused on the identification of intermediates and on the determination of the formation mechanisms of *N*-methylaniline, *N*,*N*-dimethylaniline, and toluidines. To refine the main steps of the reaction, the transformations of the following individual compounds and intermediates, which were detected in the course of alkylation, were studied: dimethyl ether, surface methoxy groups, methylanilinium ions, formaldehyde, and *N*-methyleneaniline. It was found that *N*-methylaniline and *N*,*N*-dimethylaniline were formed as a result of aniline methylation by methanol dehydration products (methoxy groups or dimethyl ether) on acidic zeolites or as a result of alkylation by formaldehyde or methoxy groups on basic zeolites. Toluidines were formed by the isomerization of *N*-methylanilinium ions, which were produced only on acidic zeolites, rather than by the direct alkylation of aniline.

INTRODUCTION

The alkylation of aniline with methanol is one of the most important industrial processes. In this case, methylation at the N-position is of greatest interest because the resulting *N*-methylaniline and *N*,*N*-dimethylaniline are used in pharmaceutical and agricultural industries.

Commercial alkylation catalysts, primarily, Friedel–Crafts reaction catalysts and mineral acids, are responsible for the corrosion of apparatus and the formation of by-products, harmful wastes, and wastewater; they require thorough purification of parent reactants. Because of this, they should be replaced by better heterogeneous catalysts. Zeolites are promising catalysts for alkylation [1–4], however, their selectivity is low. Thus, it is of importance to reveal the mechanisms of target and side reactions in the course of alkylation on zeolite catalysts of different types.

In recent years, *in situ* NMR spectroscopy has been successfully used for studying the mechanisms of reactions catalyzed by zeolites [5–10]. This technique provides an opportunity to identify reaction intermediates and to follow their transformations.

The aim of this work was to study the reaction mechanism of aniline alkylation with methanol on acidic and basic zeolites using *in situ* ^{13}C NMR spectroscopy.

EXPERIMENTAL

Zeolites HY (decationation degree of 99%) and CsNaY modified with cesium hydroxide (CsNaY–CsOH; the ion-exchange degree of sodium for cesium was 70%, and the CsOH content was 11.3 wt %) were used as catalysts. The preparation and characterization of catalyst samples were described in detail elsewhere [11, 12, 14].

The reaction mechanism of aniline methylation was studied by *in situ* NMR spectroscopy under batch and flow conditions. In batch experiments, air-dry catalyst samples (from 0.08 to 0.10 g) were placed in ampules, evacuated to 10^{-5} Torr at 673 K, and cooled to 298 K; next, the adsorption of reactants was performed. Methanol (ICON Services), dimethyl ether (Cambridge Isotope Laboratories), and paraformaldehyde (Sigma–Aldrich), all with a ^{13}C-isotope enrichment of 99%, as well as unlabeled aniline (Promochem), were used as the reactants. The surface coverage with reactants was varied from 1 to 40 molecules per zeolite unit cell (UC). After the adsorption, the ampules were cooled to 77 K, sealed off, and placed in a standard MAS NMR rotor (d = 7 mm). The reaction procedure included the heating of the ampule to a required temperature for a fixed time. For this purpose, a furnace was used, which allowed us to rapidly increase the temperature. The NMR spectra were recorded at 298 K after rapidly cooling the ampule with the sample. After recording the spectrum, the ampule was placed in the furnace once again, and the experiment was continued. This procedure was described in more detail elsewhere [13, 14].

A rotor with an axial hole in the rotor cap and with a glass tube axially placed in the rotor was used in experiments under flow conditions. In this case, the cat-

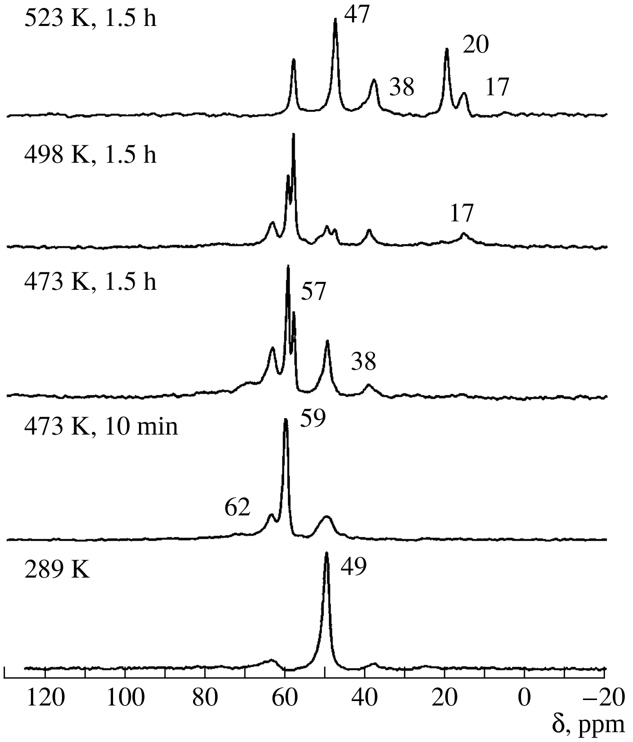

Fig. 1. ^{13}C MAS NMR spectra measured in a flow system in the course of the reaction of aniline alkylation with ^{13}C-methanol on zeolite Y under conditions of a stepwise increase in the temperature at a reactant supply rate of 0.025 mol g^{-1} h^{-1} and the molar ratio ^{13}C-methanol/aniline = 2 : 1.

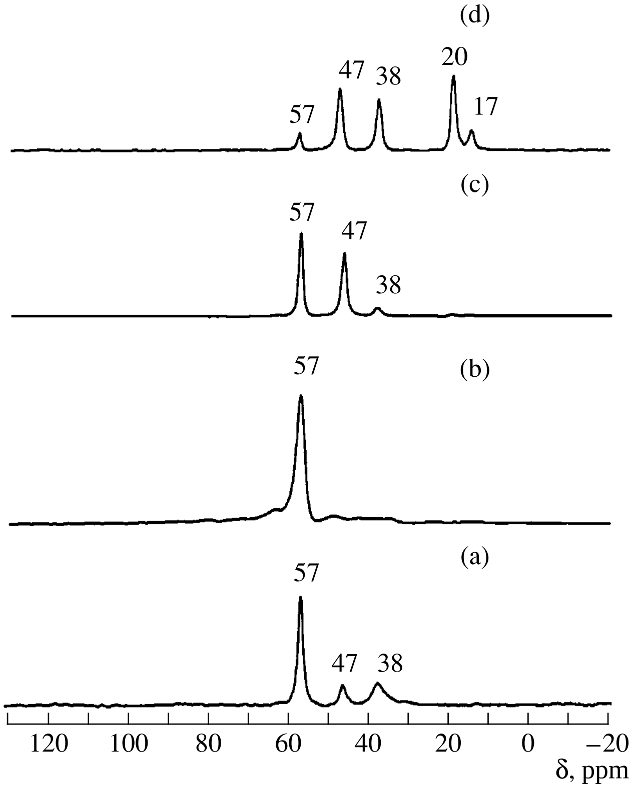

Fig. 2. ^{13}C MAS NMR spectra measured in a flow system at different stages of the experiment: (a) in the course of the reaction of ^{13}C-methanol with aniline at 473 K, a supply rate of 0.013 mol g^{-1} h^{-1}, and the molar ratio ^{13}C-methanol/aniline = 4 : 1; (b) after stopping the flow of reactants and purging the reactor with nitrogen at 298 K; and after stopping the carrier-gas flow and increasing the temperature up to (c) 498 and (d) 523 K.

alyst bed had the shape of a hollow cylinder. The reactants were injected with a carrier gas via the axially placed tube at rates of 0.013–0.025 mol g^{-1} h^{-1}, and the ^{13}C-methanol/aniline molar ratios were varied from 4 : 1 to 2 : 1. The NMR spectra were measured in the course of the catalytic reaction. The experimental procedure was detailed elsewhere [15].

The stopped-flow (SF) MAS NMR technique [19] was also used in this study. This technique consists in that the flow of reactants is stopped in the course of reaction and the reactor is purged with gaseous nitrogen; thereafter, compounds that are strongly adsorbed on the catalyst surface can be detected. To identify these compounds as reaction intermediates, the flow of one of the reactants, for example, aniline, is resumed.

The NMR spectra were measured on Bruker MSL-300 and MSL-400 spectrometers in the experiments under batch conditions and in the flow reactor, respectively. Different standard compounds were used for calibration: ^{13}C-glycine (the chemical shift δ = 176.03 ppm for the carbonyl group with reference to tetramethylsilane) on the Bruker MSL-300 spectrometer and ^{13}C-methanol (δ = 50.5 ppm for the carbon atom of the methyl group) on the Bruker MSL-400 spectrometer. The ^{13}C NMR spectra were measured both with and without ^{13}C–^{1}H spin–spin decoupling. In a number of cases, ^{13}C–^{1}H cross-polarization experiments were performed. The figures demonstrate the spectra recorded with ^{13}C–^{1}H spin–spin decoupling, unless otherwise specified.

RESULTS AND DISCUSSION

Aniline Alkylation by Methanol on Zeolite HY

Figure 1 demonstrates the ^{13}C MAS NMR spectra obtained under flow conditions on acidic zeolite HY. The initial spectrum measured at room temperature contained a signal with δ = 49 ppm, which corresponds to the carbon atom of the methyl group of methanol. The signal was accompanied by spinning sidebands; this fact suggested that methanol was strongly adsorbed on the catalyst surface. The signals that corresponded to the carbon atoms of the aromatic ring of aniline were weak (because unlabeled aniline was used) and strongly broadened because of aniline protonation at the acid sites of the zeolite [14].

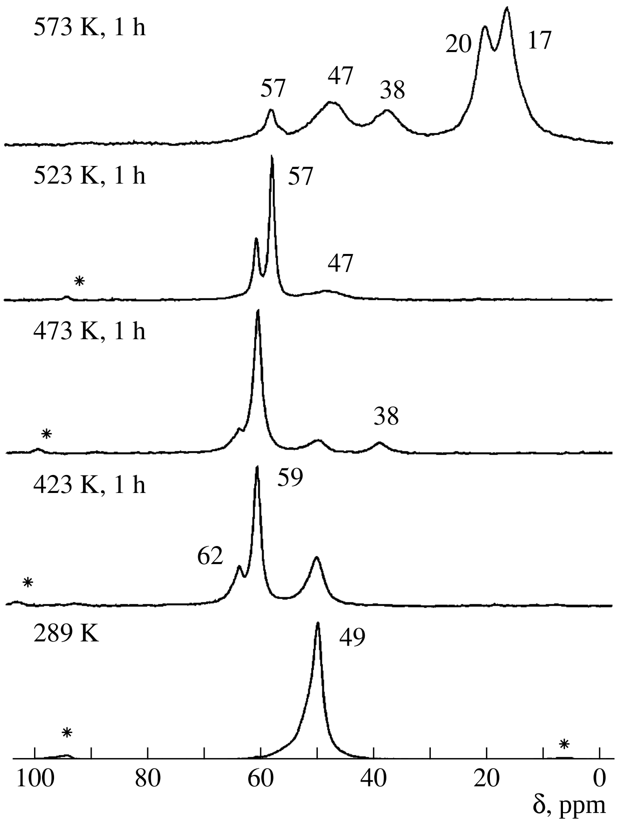

Fig. 3. ^{13}C MAS NMR spectra measured under conditions of a stepwise increase in the temperature in the course of the reaction of aniline with ^{13}C-methanol on zeolite HY in a batch mode after the adsorption of ^{13}C-methanol (40 molecule/UC) and aniline (10 molecule/UC).

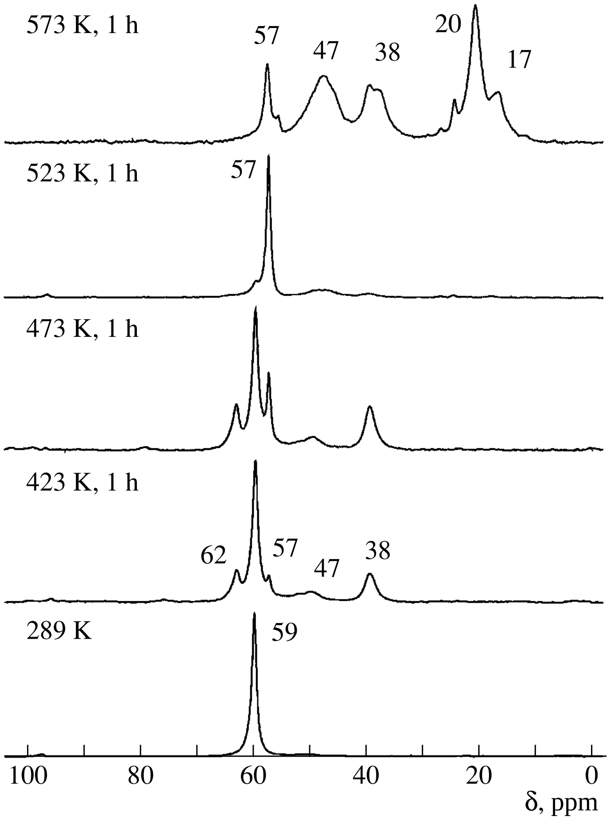

Fig. 4. ^{13}C MAS NMR spectra measured under conditions of a stepwise increase in the temperature in the course of the reaction of aniline with ^{13}C-dimethyl ether on zeolite HY in a batch mode after the adsorption of ^{13}C-dimethyl ether (20 molecule/UC) and aniline (10 molecule/UC).

At 473 K, signals with δ = 59 and 62 ppm were detected, which corresponded to different species of dimethyl ether (DME) adsorbed on zeolite HY [16]. A further heating at 473 K resulted in the appearance of signals with δ = 38 and 57 ppm. The former signal was attributed to the methyl group of *N*-methylaniline, as supported by a special experiment with *N*-methylaniline adsorbed on zeolite HY. A considerable downfield shift of the signal of adsorbed *N*-methylaniline, as compared with the results obtained with this compound in a liquid phase (δ = 29.9 ppm [17]), was explained by the protonation of the NH groups of *N*-methylaniline by the Brönsted acid sites of the zeolite and the formation of *N*-methylanilinium ions on the zeolite surface.

The signal with δ = 57 ppm was attributed to the methyl group of the *N*,*N*,*N*-trimethylanilinium ion [18]. As the system was further heated to 498 and 523 K, the intensity of this signal initially increased and then decreased. In this case, the intensities of peaks due to *N*-methylanilinium (δ = 38 ppm) and *N*,*N*-dimethylanilinium (δ = 47 ppm), which was also downfield shifted with respect to *N*,*N*-dimethylaniline (δ = 40.3 ppm [17]), simultaneously increased. At elevated temperatures, signals attributed to aromatic ring substitution products (*ortho*-, *para*-, and *meta*-toluidines) were detected in the spectra (δ = 17–20 ppm) in addition to the signals due to N-alkylation products.

An experiment with the use of the SF ^{13}C MAS NMR technique [18] was performed for elucidating the role of the *N*,*N*,*N*-trimethylanilinium ion in the alkylation reaction of aniline. Figure 2 demonstrates the results of this experiment. At the first stage of the experiment under flow conditions at 473 K, the reaction of ^{13}C-methanol and aniline was performed with the formation of N-methylation products (*N*-methylanilinium and *N*,*N*-dimethylanilinium in small amounts and *N*,*N*,*N*-trimethylanilinium in a considerable amount) (Fig. 2a). At the next stage, the supply of the reactants to the reactor was stopped, and the temperature was decreased to room temperature with continuously purging the reactor with nitrogen. As a result, a signal due to the *N*,*N*,*N*-trimethylanilinium ion was observed (Fig. 2b). After stopping the carrier-gas flow and the subsequent heating of the system to 498 K, the *N*,*N*,*N*-trimethylanilinium ion was converted into *N*-methylanilinium and *N*,*N*-dimethylanilinium and further into toluidines at 523 K (Figs. 2c, 2d). Thus, we found that

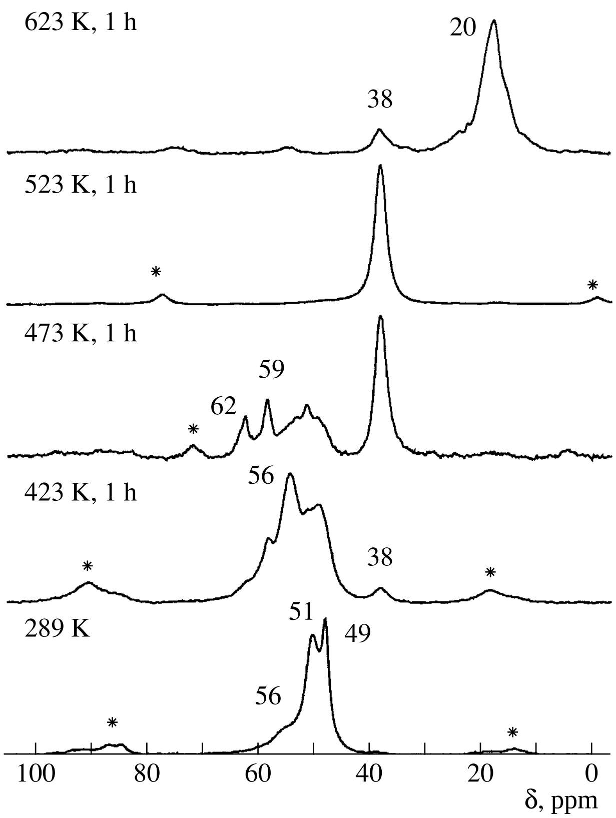

Fig. 5. ^{13}C MAS NMR spectra measured under conditions of a stepwise increase in the temperature in the course of the reaction of aniline with ^{13}C-methanol on zeolite HY in a batch mode after the adsorption of ^{13}C-methanol (7 molecule/UC) and aniline (21 molecule/UC).

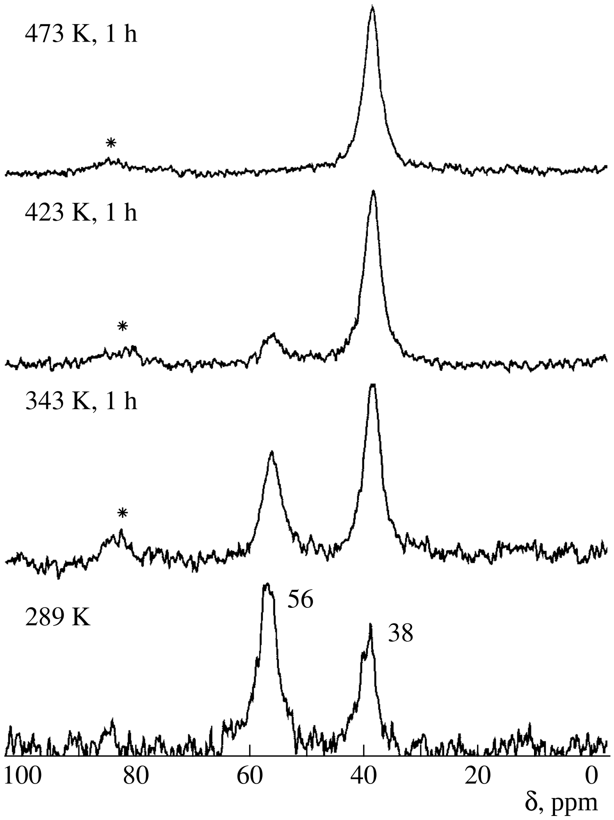

Fig. 6. ^{13}C MAS NMR spectra measured under conditions of a stepwise increase in the temperature in a batch mode in the course of aniline (21 molecule/UC) conversion on zeolite HY methoxylated with ^{13}C-methyl iodide.

the decomposition of the *N*,*N*,*N*-trimethylanilinium ion gives N- and C-methylation products.

Figure 3 demonstrates the ^{13}C MAS NMR spectra obtained under batch conditions at high surface coverages (θ) with the reactants in a considerable excess of methanol over aniline. A comparison of Figs. 1 and 3 suggests that the course of the reaction and the intermediate compounds detected under batch conditions were identical to those found in the flow system. However, the sequence of reaction steps was more clearly revealed under batch conditions. Thus, we found that *N*-methylanilinium ($\delta = 38$ ppm) is the primary reaction product, whereas *N*,*N*-dimethylanilinium ($\delta = 47$ ppm) and *N*,*N*,*N*-trimethylanilinium ($\delta = 57$ ppm) result from the further methylation of aniline.

The experimental results obtained under flow and batch conditions in an excess of methanol suggest that DME can play the role of an intermediate compound in the course of N-methylation. To test this hypothesis, we studied the reaction of DME with aniline under batch conditions at the molar ratio ^{13}C-DME/aniline = 2 : 1. After heating the system to 423 K, signals with $\delta = 38$, 47, and 57 ppm appeared, which were ascribed to *N*-methylanilinium, *N*,*N*-dimethylanilinium, and *N*,*N*,*N*-trimethylanilinium ions, respectively (Fig. 4). This result indicates that DME acts as an alkylating agent in the course of *N*-methylation.

Figure 5 demonstrates the spectra obtained under batch conditions at low surface coverages with methanol and aniline. Note that the shapes of the spectra were different from that observed in experiments with high values of θ (Figs. 1, 3). Even at room temperature, two additional signals with $\delta = 51$ and 56 ppm were detected along with a signal with $\delta = 49$ ppm, which corresponds to methanol adsorbed on the surface of zeolite HY. These signals were attributed to the adsorption complex of methanol with aniline and to the surface methoxy group, respectively [14].

The heating of the system to 423 K resulted in an increase in the signal due to the methoxy group and in the formation of a small amount of DME. A signal due to *N*-methylanilinium ($\delta = 38$ ppm) appeared simultaneously. As the temperature was further increased, the signal intensity of the methoxy group dramatically decreased, whereas the signal intensity of *N*-methylanilinium increased. Thus, the results obtained at low θ

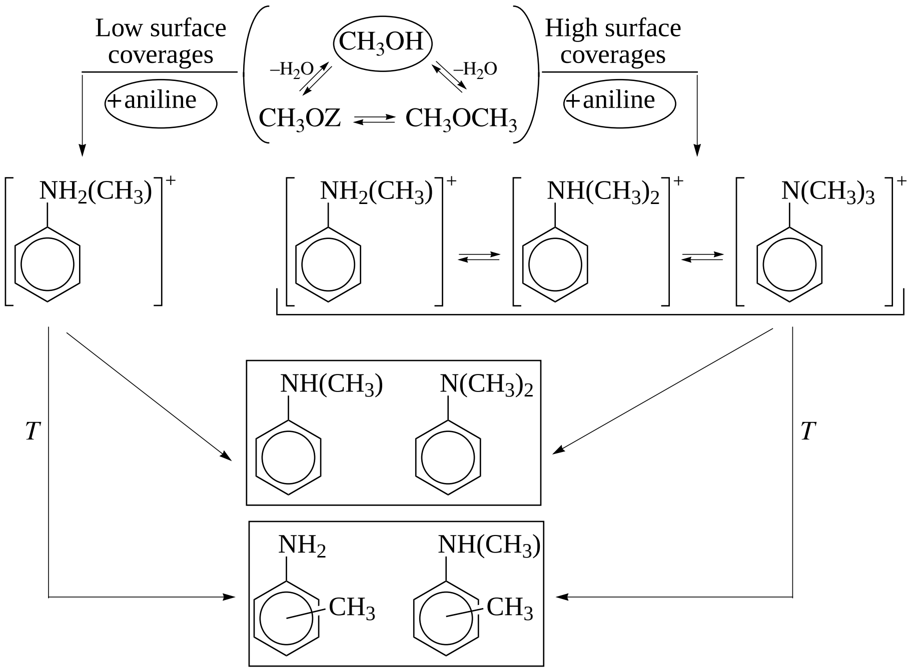

Fig. 7. Schematic diagram of aniline alkylation by methanol on acidic zeolite HY.

provide support to the hypothesis that methoxy groups take part in N-alkylation.

This hypothesis was tested in a study of the interaction of aniline with zeolite HY pretreated with ^{13}C-methyl iodide (Fig. 6). In addition to a signal with δ = 56 ppm, which corresponds to the methoxy group, the initial spectrum exhibited an intense peak with δ = 38 ppm, which suggests the formation of *N*-methylanilinium. Consequently, methoxy groups are capable of the N-methylation of aniline even at room temperature. A subsequent increase in the temperature to 343 and 423 K resulted in an increase in the signal intensity of *N*-methylanilinium with a simultaneous decrease in the signal intensity of the methoxy group. At 473 K, a peak with δ = 56 ppm was not detected; that is, methoxy groups were completely converted into *N*-methylanilinium ions.

Note that, in all the experiments, signals due to toluidines within the range δ = 17–20 ppm appeared at elevated temperatures even after the complete conversion of methylating agents (Figs. 1–5). This finding indicates that, in contrast to *N*-methylanilines, toluidines resulted from the isomerization of *N*-methylanilinium ions rather than from the direct alkylation of aniline.

Figure 7 represents a schematic diagram of aniline alkylation with methanol on zeolite HY based on NMR-spectroscopic data. At low values of θ, surface methoxy groups were formed as a result of methanol dehydration. These groups readily methylated aniline with the intermediate formation of *N*-methylanilinium ions; *N*-methylaniline resulted from the deprotonation of these ions. At high surface coverages and a methanol-to-aniline concentration ratio of 4 : 1, the dehydration was accompanied by the formation of DME. The methylation of aniline by DME occurred via the consecutive formation of *N*-methylanilinium, *N*,*N*-dimethylanilinium, and *N*,*N*,*N*-trimethylanilinium ions, which decomposed to give *N*-methylaniline and *N*,*N*-dimethylaniline. Toluidines were formed as secondary products by the isomerization of *N*-methylanilinium ions.

Aniline Alkylation by Methanol on Zeolite CsOH/CsNaY

Figure 8 demonstrates the ^{13}C MAS NMR spectra measured in the course of the reaction of ^{13}C-methanol with aniline on basic zeolite CsOH/CsNaY under flow conditions at a methanol/aniline molar ratio of 4 : 1. The initial spectrum, which was measured at room temperature after supplying the reactants, exhibited one signal with δ = 49 ppm (Fig. 8a), which is characteristic of the methyl group of methanol. As the temperature was increased up to 498 K (Fig. 8b), this signal exhibited a shoulder with δ = 52–53 ppm due to the formation of the methoxy group on the zeolite surface. Moreover, three new lines were also detected in the spectrum: an intense signal with δ = 157 ppm and two weak signals with δ = 38 and 167 ppm, which were attributed to the methylene group in *N*-methyleneaniline, the methyl group in *N*-methylaniline, and the carbon atom in the formate group immobilized on the zeolite surface, respectively [19]. Note that, in contrast to the acidic zeolite, the chemical shift of the signal corresponding to the methyl group of *N*-methylaniline on the

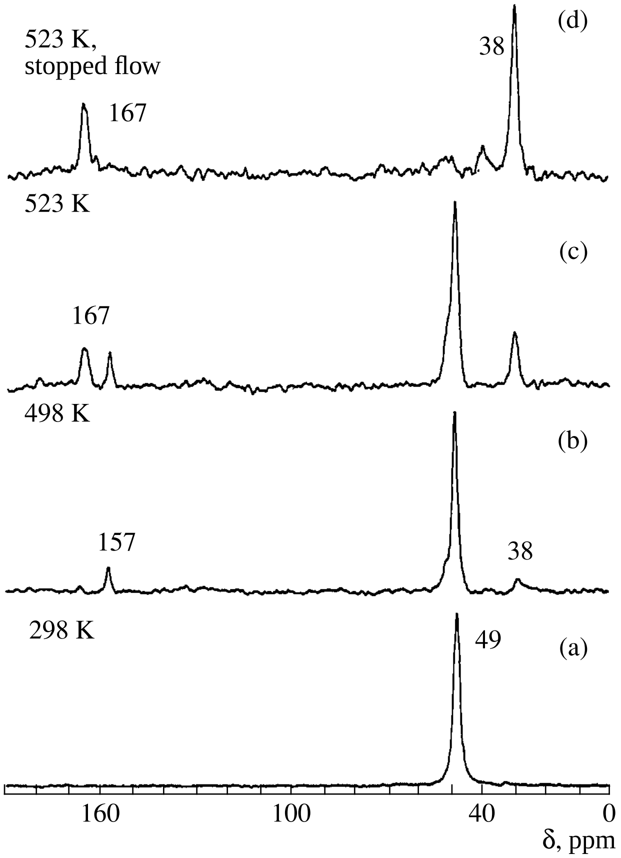

Fig. 8. ^{13}C MAS NMR spectra measured in the course of the reaction of aniline alkylation with ^{13}C-methanol on zeolite CsOH/CsNaY under flow conditions at a reactant supply rate of 0.025 mol g^{-1} h^{-1} and the molar ratio ^{13}C-methanol/aniline = 4 : 1 (a–c) during a stepwise increase in the temperature from 298 to 523 K and (d) after stopping the flow of reactants at 523 K.

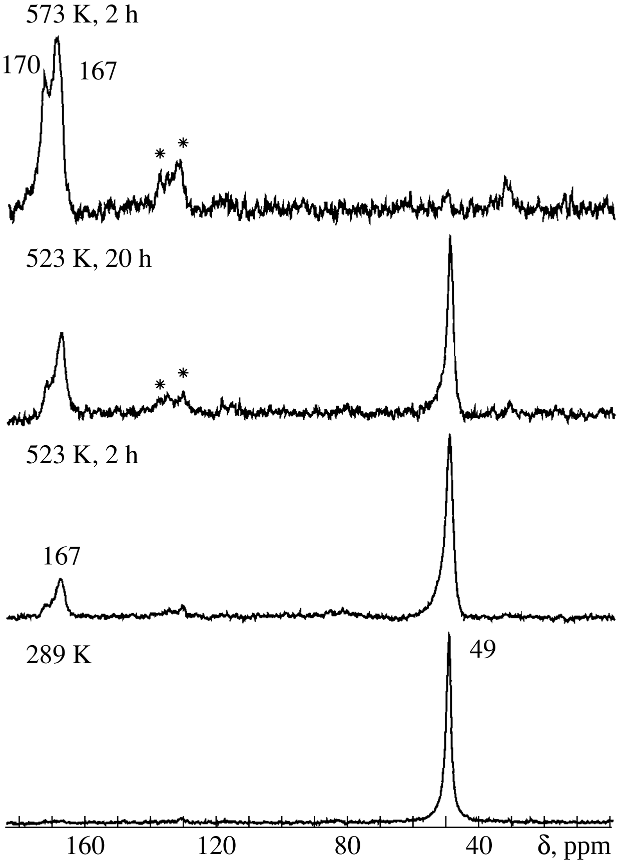

Fig. 9. ^{13}C MAS NMR spectra measured during a stepwise increase in the temperature in the course of the reaction of aniline and ^{13}C-methanol on zeolite CsOH/CsNaY under batch conditions after the adsorption of ^{13}C-methanol (1.5 molecule/UC) and aniline (2.5 molecule/UC).

basic zeolite was close to the chemical shift of this compound obtained in a liquid [17].

A further increase in the reaction temperature up to 523 K increased the intensities of signals due to *N*-methylaniline and the formate group. The signal intensity of *N*-methyleneaniline passed through a maximum; this fact is indicative of the intermediate formation of this compound. After stopping the flow of reactants in the SF ^{13}C MAS NMR experiment, *N*-methyleneaniline was completely converted into *N*-methylaniline (Fig. 8d). Therefore, *N*-methyleneaniline is an intermediate product in the formation of *N*-methylaniline.

The appearance of *N*-methyleneaniline in the course of the reaction can be explained by the alkylation of aniline with formaldehyde, which is a product of methanol dehydration on the basic zeolite. The appearance of a signal with $\delta = 167$ ppm also suggests the intermediate formation of formaldehyde; this signal belongs to the surface formate group, which may result from a parallel reaction path in formaldehyde conversion. An analogous mechanism of alkylation on basic zeolites was proposed by Sidorenko and Galich [20] for the reaction of toluene methylation to ethylbenzene; this mechanism was supported by a number of more recent studies [21–23].

The reaction of aniline methylation at low values of θ and low methanol-to-aniline ratios was studied under batch conditions. Figures 9 and 10 demonstrate the results. In contrast to the experiments performed with an excess of methanol (Fig. 8), the signal that corresponds to *N*-methyleneaniline was not detected. This suggested that other reaction paths of aniline methylation can occur on the basic zeolite, and the path with the intermediate formation of *N*-methyleneaniline is only one of them.

It is of importance that the direction of reaction under batch conditions strongly depended on the catalyst surface coverage with reactants. On the adsorption of 1.5 molecules of methanol and 2.5 molecules of aniline per UC of the zeolite (Fig. 9), methanol was almost completely converted into surface formate groups, which are characterized by signals with $\delta = 167$ and 170 ppm [22]. The product of aniline alkylation,

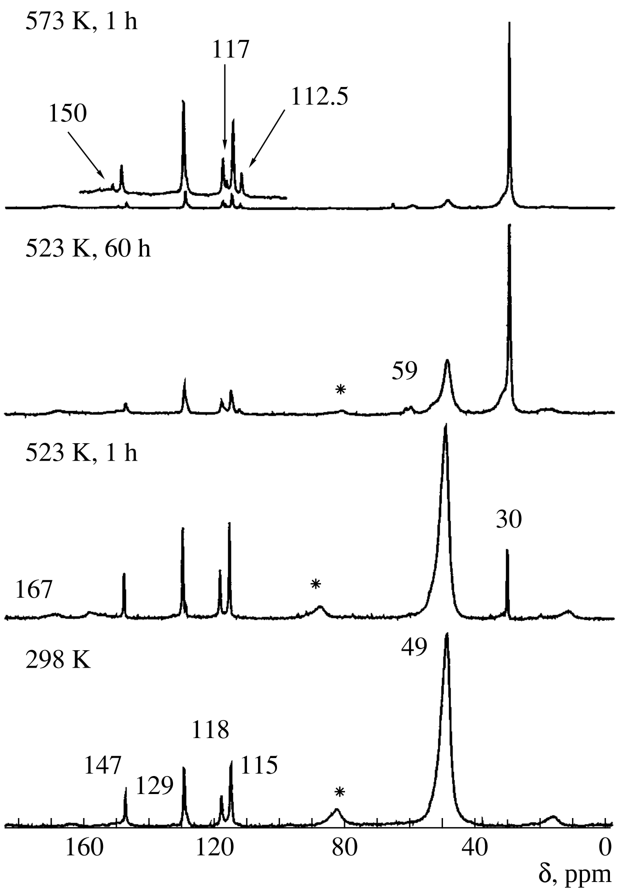

Fig. 10. ^{13}C MAS NMR spectra measured during a stepwise increase in the temperature in the course of the reaction of aniline and ^{13}C-methanol on zeolite CsOH/CsNaY under batch conditions after the adsorption of ^{13}C-methanol (7 molecule/UC) and aniline (21 molecule/UC).

N-methylaniline, was detected only in trace amounts. It is likely that, at these low surface coverages, the probability of collisions between reactant molecules is low. Indeed, the number of basic sites in zeolite CsOH/CsNaY was ~14 per UC; this value was several times greater than the number of adsorbed molecules.

On the contrary, on the adsorption of 7 molecules of methanol and 21 molecules of aniline, the main reaction path was alkylation to *N*-methylaniline (Fig. 10), as evidenced by the appearance of an intense signal with δ = 30 ppm, which was due to the labeled methyl group of *N*-methylaniline, and by the appearance of weak lines with δ = 112.5, 117, and 150 ppm, which corresponded to carbon atoms of the unlabeled aromatic ring of *N*-methylaniline. At elevated temperatures and considerable heating times (523 K, 60 h and 573 K, 1 h), the spectra exhibited a signal with δ = 40 ppm, which corresponded to the formation of a small amount of *N*-dimethylaniline. In this case, the products of further N-methylation and the products of alkylation at the aromatic ring (toluidines) were not detected.

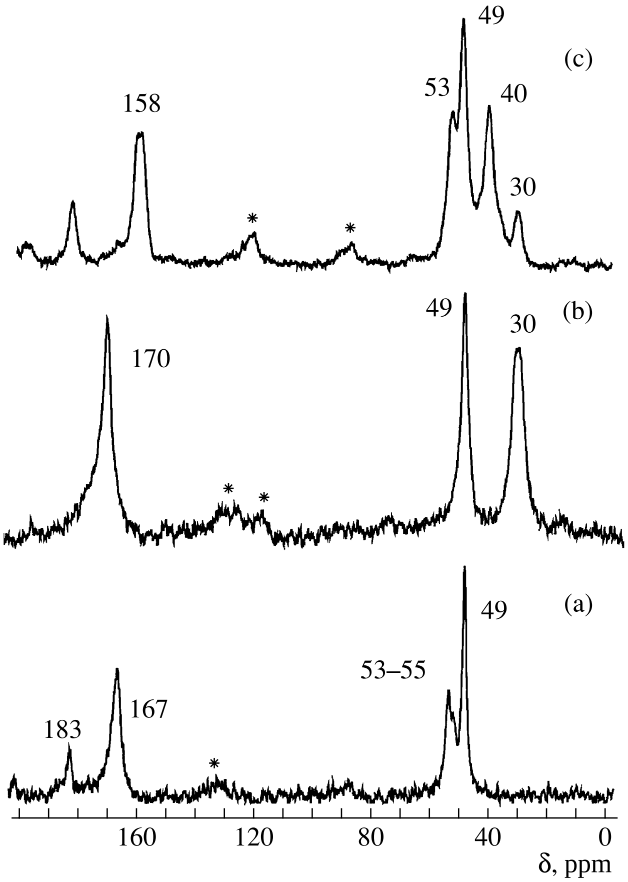

Fig. 11. ^{13}C MAS NMR spectra measured in the course of the reaction of ^{13}C-formaldehyde and aniline on zeolite CsOH/CsNaY under batch conditions at different catalyst surface coverages with reactants: (a) after the adsorption of formaldehyde (7 molecule/UC) at 298 K, (b) after the adsorption of formaldehyde (7 molecule/UC) and aniline (21 molecule/UC) and heating the system at 423 K for 1 h, and (c) after the adsorption of formaldehyde (40 molecule/UC) and aniline (10 molecule/UC) and heating the system at 423 K for 1 h.

The methylation of aniline by methoxy groups can be one of the conceivable reaction paths resulting in the formation of methylanilines on basic zeolites at low surface coverages. Indeed, the intermediate formation of a small amount of methoxy groups was detected, as evidenced by the appearance of a shoulder in the signal with δ = 49 ppm, whose intensity increased in experiments with the use of the cross-polarization technique. It is unlikely that the appearance of methoxy groups on basic zeolites can be due to methanol dehydration, as it was the case in acidic zeolites. It is most likely that this resulted from formaldehyde disproportionation. However, this hypothesis required an experimental support.

An analysis of the results obtained under both flow and batch conditions indirectly suggests that methanol underwent dehydration to form formaldehyde, which is an intermediate species in all the subsequent transformations, at the first step of the reaction on the basic zeo-

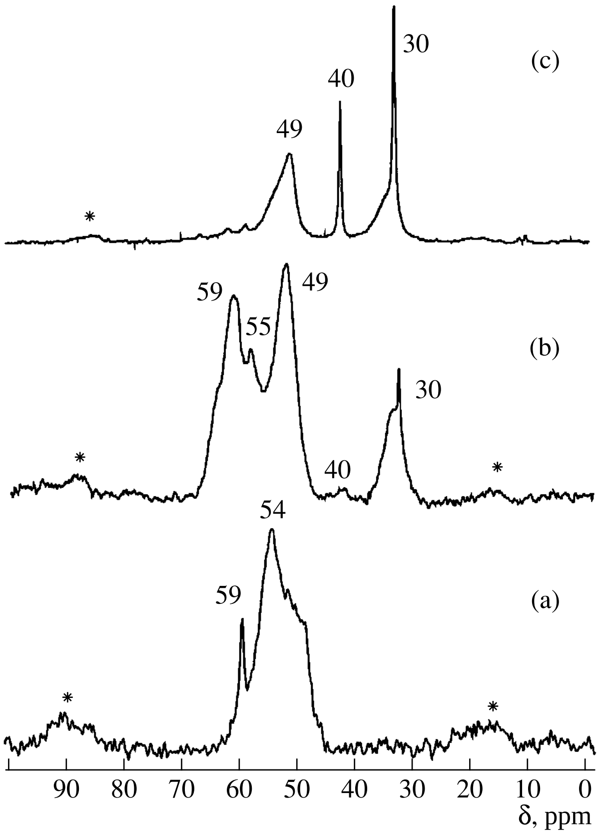

Fig. 12. ^{13}C MAS NMR spectra measured in the course of aniline conversion on zeolite CsOH/CsNaY methoxylated with ^{13}C-methyl iodide (7 molecule/UC): (a) immediately after the methoxylation of the catalyst surface at 298 K, (b) after the subsequent adsorption of aniline (21 molecule/UC) at 298 K, and (c) after heating the system to 423 K.

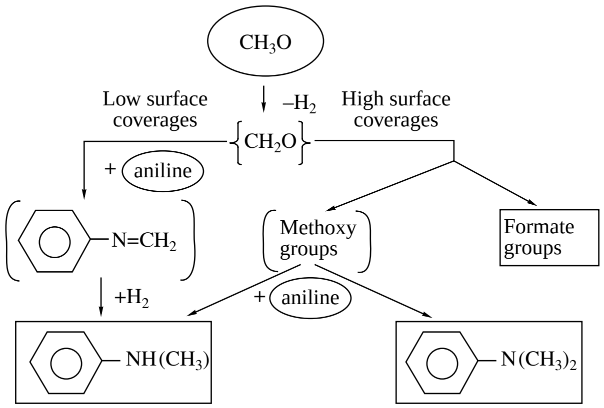

Fig. 13. Schematic diagram of aniline alkylation by methanol on basic zeolite CsOH/CsNaY. Intermediates detected in the course of NMR experiments are given in parentheses. Hypothetical intermediates based on indirect data are given in braces.

lite. To test this hypothesis, we studied the conversion of formaldehyde and its mixture with aniline under batch conditions at different surface coverages. Figure 11 demonstrates the results.

On the adsorption of 7 molecules of formaldehyde per UC, it underwent rapid disproportionation even at room temperature. The NMR spectrum (Fig. 11a) exhibited signals due to adsorbed CO (δ = 183 ppm), the formate group (δ = 167 ppm), the methoxy group (δ = 53 ppm), and methanol (δ = 49 ppm). The numbers of the resulting methanol molecules and methoxy groups were much the same as the numbers of CO molecules and formate groups.

On the adsorption of 7 molecules of formaldehyde and 21 molecules of aniline per UC of the zeolite and on heating this system to 423 K, a signal with δ = 30 ppm, which corresponds to *N*-methylaniline, appeared and a signal due to methoxy groups disappeared (Fig. 11b). The signal that corresponded to *N*-methyleneaniline was not observed.

In an experiment with high values of θ (Fig. 11c), along with signals corresponding to CO, methanol, and the methoxy group, signals from *N*-methyleneaniline (δ = 158 ppm), *N*-methylaniline (δ = 30 ppm), and *N*-dimethylaniline (δ = 40 ppm) were detected.

Thus, the experiments with formaldehyde demonstrated that the direct interaction of formaldehyde with aniline followed by the hydrogenation of the resulting *N*-methyleneaniline to *N*-methylaniline was most probable at high surface coverages, whereas aniline alkylation by methoxy groups formed by the disproportionation of formaldehyde was most probable at low surface coverages.

To verify the participation of methoxy groups in alkylation and to determine their reactivity, we studied the interaction of aniline with zeolite CsOH/CsNaY methoxylated with ^{13}C-methyl iodide. Figure 12a demonstrates the NMR spectrum obtained after the adsorption of 7 molecules of $^{13}CH_3I$. The results suggest that methyl iodide that reacted with the zeolite surface was completely converted into methoxy groups (δ = 51–54 ppm), methanol (δ = 49 ppm), and DME (δ = 59 ppm); in this case, methoxy groups gave the main contribution to the spectrum. The subsequent adsorption of aniline resulted in the appearance of an intense signal with δ = 30 ppm and a weak signal at 40 ppm, which are characteristic of *N*-methylaniline and *N*-dimethylaniline, respectively (Fig. 12b). An increase in the temperature to 423 K increased the intensities of signals due to N-alkylation products, and signals in the range δ = 52–60 ppm disappeared (Fig. 12c). Thus, we found that, as in the case of the reaction on the acidic zeolite, methoxy groups are highly reactive species, which are responsible for methylation at the N-position, on the basic zeolite.

Figure 13 depicts a schematic diagram of processes that occurred on the surface of zeolite CsOH/CsNaY; this diagram is based on our spectroscopic data. Methanol dehydration is the first and rate-limiting step of the reaction. The resulting formaldehyde is highly reactive, and its signal was not detected in the course of a direct *in situ* NMR experiment. However, all the indirect data suggest that it plays an intermediate role in all the subsequent steps. At high surface coverages with reactants, the alkylation of aniline by formaldehyde took place with the formation of *N*-methyleneaniline, which was hydrogenated to *N*-methylaniline with hydrogen, which was formed at the first step of the reaction. At low values of θ, formaldehyde was converted into surface formate and methoxy groups. These latter are active alkylating species, and the alkylation reaction with the participation of these species occurs even at room temperature. A characteristic property of methoxy groups as alkylating species consists in that they can form both mono- and dimethylanilines, whereas only monomethylation by the addition of a methylene group is possible in the case of formaldehyde.

Thus, we experimentally found that different alkylation mechanisms occurred on the acidic and basic forms of zeolite Y. These mechanisms included the intermediate formation of DME, methoxy groups, and methylanilinium ions in the former case and formaldehyde, *N*-methylaniline, and methoxy groups in the latter case.

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REFERENCES

1. Narayanan, S. and Deshpande, K., *Appl. Catal., A*, 2000, vol. 199, p. 1.
2. Narayanan, S., Durga Kumari, V., and Sudhakar Rao, A., *Appl. Catal., A*, 1994, vol. 111, p. 133.
3. Park, Y.K., Park, K.Y., and Woo, S.I., *Catal. Lett.*, 1994, vol. 26, p. 169.
4. Hari Prasad Rao, P.R., Massiani, P., and Barthomeuf, D., *Catal. Lett.*, 1995, vol. 31, p. 115.
5. Klinowski, J., Thomas, J.M., Audier, M., Vasudevan, S., Fyfe, C.A., and Hartman, J.S., *J. Chem. Soc., Chem. Commun.*, 1981, p. 570.
6. Anderson, M.V. and Klinowski, J., *Nature*, 1989, vol. 339, p. 200.
7. Haw, J.F., *NMR Techiques in Catalysis*, New York: Marcel Dekker, 1994, p. 139.
8. Hunger, M. and Horvath, T., *J. Chem. Soc., Chem. Commun.*, 1995, p. 1423.
9. Ivanova, I.I., *Ross. Khim. Zh.*, 1998, vol. 42, p. 67.
10. Stepanov, A.G., *Usp. Khim.*, 1999, vol. 68, no. 7, p. 619.
11. Hunger, M., Schenk, U., and Weitkamp, J., *Angew. Chem., Int. Ed. Engl.*, 1997, vol. 63, p. 2504.
12. Hunger, M., Schenk, U., Seiler, M., and Weitkamp, J., *J. Mol. Catal. A: Chem.*, 2000, vol. 156, p. 153.
13. Derouane, E.G., Abdul-Hamid, S.B., Ivanova, I.I., Blom, N., and Højlund-Nielsen, P.E., *J. Mol. Catal.*, 1994, vol. 86, p. 371.
14. Ivanova, I.I., Pomakhina, E.B., Rebrov, A.I., Hunger, M., Kolyagin, Y.G., and Weitkamp, J., *J. Catal.*, 2001, vol. 203, p. 375.
15. Hunger, M., Seiler, M., and Horvath, T., *Catal. Lett.*, 1999, vol. 57, p. 199.
16. Ivanova, I.I. and Corma, A., *J. Phys. Chem.*, 1997, vol. 101, p. 547.
17. Breitmaier, E. and Voelter, W., *Carbon-13 NMR Spectroscopy*, Weinheim: VCH, 1987, p. 257.
18. Wang, W., Seiler, M., Ivanova, I.I., Sternberg, U., Weitkamp, J., and Hunger, M., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 7548.
19. Wang, W., Seiler, M., Ivanova, I.I., Weitkamp, J., and Hunger, M., *J. Chem. Soc., Chem. Cummun.*, 2001, p. 1362.
20. Sidorenko, Yu.N. and Galich, P.N., *Ukr. Khim. Zh.*, 1970, vol. 36, p. 1234.
21. Itoh, H., Miayamoto, A., and Murakami, Y., *J. Catal.*, 1980, vol. 64, p. 284.
22. Philippou, A. and Anderson, M.W., *J. Am. Chem. Soc.*, 1994, vol. 116, p. 5774.
23. Hunger, M., Schenk, U., and Weitkamp, J., *J. Mol. Catal., A: Chem.*, 1998, p. 97.