Solid-State NMR Investigation of the Alkylation of Toluene with Methanol over Basic Zeolite X

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Abstract: The alkylation of toluene with methanol over different alkali-metal cation forms of zeolite X has been studied by ^{13}C solid-state NMR with magic-angle spinning (MAS NMR). The catalysts used were Na-X, K-X, and Cs-X. The results indicate that the fate of the methanol, both in terms of surface complexation and decomposition, plays an important role in this alkylation process. The alkylation reaction starts at ca. 340 °C with complete conversion at 450 °C. A number of resonances corresponding to species not observed in the product stream appear before and during the formation of products. All of these lines have been assigned and indicate the presence of surface bound methoxy ions and surface formates. Formaldehyde is suggested to be the alkylating agent for side-chain alkylation while methyl carbocations are responsible for ring alkylation. Over Na-X protonated metal methoxy species are observed and are the source of methyl carbocations. These surface complexes are found to a lesser extent in K-X and are not formed in Cs-X. Over Cs-X the interaction of methanol with the basic sites results in the formation of formaldehyde. In addition, methyl carbocations can be formed during the formation of the surface formates observed in all three catalysts. It is found that in Cs-X the zeolite plays a crucial role gettering these highly reactive carbocations by binding them as surface bound methoxy groups. This prevents ring alkylation occurring on Cs-X.

Introduction

Base-catalyzed reactions over zeolites,[1,2] although of great importance, have received considerably less attention than acid-catalyzed reactions. While it is known that alkali cation exchanged zeolites are not very active for the promotion of reactions proceeding via carbonium ions, they are very active for reactions such as dehydration of alcohols,[3] dealkylation of cumene,[4] and alkylation of toluene.[5,6]

Alkylation of toluene with methanol over zeolite catalysts[7] can produce ethylbenzene, styrene, and/or xylenes depending upon the acidity of the catalyst and the pore size of the molecular sieve. Medium-pore acidic zeolites, e.g. H-ZSM-5, favor ring alkylation[8–10] while large-pore basic zeolites, e.g. K-X, favor side-chain alkylation.[5,6,11] In the present work we are mainly concerned with the side-chain alkylation over alkali-metal exchanged X-type zeolites. The selectivity for side-chain alkylation versus ring alkylation increases with the size of the alkali cation. This has been correlated both with the increasing inhibition of toluene rotation in the zeolite cavity[12] and with the rise of the basic strength of the catalyst.[2,13] Quantum-chemistry calculations[14] have shown

that the presence of basic sites is important to the mechanism for side-chain alkylation. It was suggested that specific steric configurations of acidic and basic sites were crucial to the formation of reaction complexes on the zeolite surface. Further Raman and UV spectroscopic studies[15,16] on the interaction of the aromatic molecules with the alkali-metal cations showed that the increase in the electrostatic field within the supercage, for large cations, leads to an increase in the interaction with the cation. This interaction is through the π-electron cloud and has been correlated with the influence of the electrostatic field on the selectivity of these catalysts for side-chain alkylation.

The currently accepted reaction scheme[6,14,17] for side-chain alkylation is as follows: (1) dehydrogenation of methanol to formaldehyde; (2) attack of formaldehyde at the methyl group of toluene to form styrene; and (3) hydrogenation of styrene to ethylbenzene by H_2 produced during the methanol dehydrogenation.

Solid-state NMR has proven to be a powerful spectroscopic technique for probing surface species during zeolite-catalyzed reactions. A large number of reactions, catalyzed within microporous materials, have been investigated by this technique[18–26] providing detailed, quantitative information of the molecular species within the cavities of the microporous catalysts. Of particular relevance to this study is the early work of Sefcik,[12] who used NMR, without the benefits of MAS, to study absorption

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Table 1. Cation Composition (mol %) of the X-Type Zeolites

zeolite	H^{+} [a]	Na^{+}	K^{+}	Cs^{+}
Na–X	5	95		
K–X	2	4	94	
Cs–X	24	14		62

[a] H^{+} values were calculated using the difference between the Al content and the sum of the alkali-metal values recognizing that from the ^{27}Al MAS NMR spectra, not shown, only tetrahedral framework aluminum is present.

complexes of toluene and ethylbenzene and breakdown products from methanol and formaldehyde on basic zeolite X. This work is, to date, the only NMR study of relevance in this field. Our work extends these original studies by (i) investigating the reaction of methanol with toluene and (ii) using MAS to yield detailed quantitative information concerning reaction intermediates. We provide spectroscopic evidence for surface intermediates formed during the side-chain alkylation of toluene by methanol over basic zeolite X which enables us to draw conclusions regarding reaction mechanisms.

Experimental Section

Sample Preparation. Zeolite Na-X was obtained from a commercially available source (13X, with Si/Al: 1.3). Zeolite K-X and zeolite Cs-X were prepared by conventional cation-exchange procedures using 0.5 M aqueous solutions of KOH and CsOH at 343 K. All catalysts were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), [29]Si and [27]Al magic-angle spinning nuclear magnetic resonance (MAS NMR). The elemental analysis of these materials has been carried out by energy dispersive analysis of X-rays (EDAX).

Catalysis. Methanol (99% ^{13}C-enriched) obtained from the MSD isotopes was used during this series of experiments. Natural abundance ^{13}C toluene from Aldrich was used. Catalyst (50 mg) was loaded into specially designed Pyrex capsules[19] which were connected to a vacuum line. The catalysts were activated under vacuum at 673 K for 24 h and then loaded with controlled quantities of reactants. All toluene:methanol molar ratios used in this work were 3:1 and the absolute sample loadings were 14.0, 14.8, and 17.5 mol of toluene per unit cell for Na-X, K-X, and Cs-X, respectively. Similar results, however, were obtained at a ratio of 5:1. The order of loading methanol and toluene was varied. The sample capsule was then sealed under vacuum while keeping the catalyst at 77 K in order to prevent the onset of reaction. The capsule was then placed inside the NMR rotor and spun up to 4000 Hz at the magic angle to produce the spectra presented in this work. Heating of the samples was performed outside the NMR spectrometer followed by cooling to room temperature which quenched the reaction. In several cases, in order to study the binding strength of surface species the sample, after being loaded with the reactants, heated up to the reaction temperature, and then cooled under vacuum to room temperature, was evacuated vigorously before sealing as above. Catalysts were checked for thermal stability both after activation and after reaction by XRD and ^{27}Al MAS NMR.

NMR Spectroscopy. All ^{13}C MAS NMR spectra were recorded at room temperature on a Bruker MSL 400 spectrometer using a Chemagnetics APEX 400 pencil probe, specially designed for spinning sealed samples. Most of the experiments were carried out by means of single pulse direct excitation with high-power proton decoupling. Pulse delays of 5 s were found adequate to yield quantitatively reliable spectra. Where necessary spectra were recorded with cross polarization to enhance weak resonances from low abundant, strongly bound surface species. Contact times in these cases were 3 ms. Chemical shifts are referenced either to external tetramethylsilane or to the silicon rubber sleeve used to hold the spinning samples. This silicon rubber sleeve exhibited one narrow signal at a chemical shift of 1.2 ppm from TMS. [13]C spectra recorded with high-power decoupling exhibit a broad background signal near 110 ppm which disappears when recorded with cross polarization.

Results

Table 1 shows the cation contents of the catalysts studied in this work. These values were determined by EDAX and consequently will have an associated error of ca. 10%. Nevertheless, the results give a clear indication of the level of ion exchange. In all cases it was assumed that the residual cation balance, after considering the alkali-metal cation, was accommodated by protons.
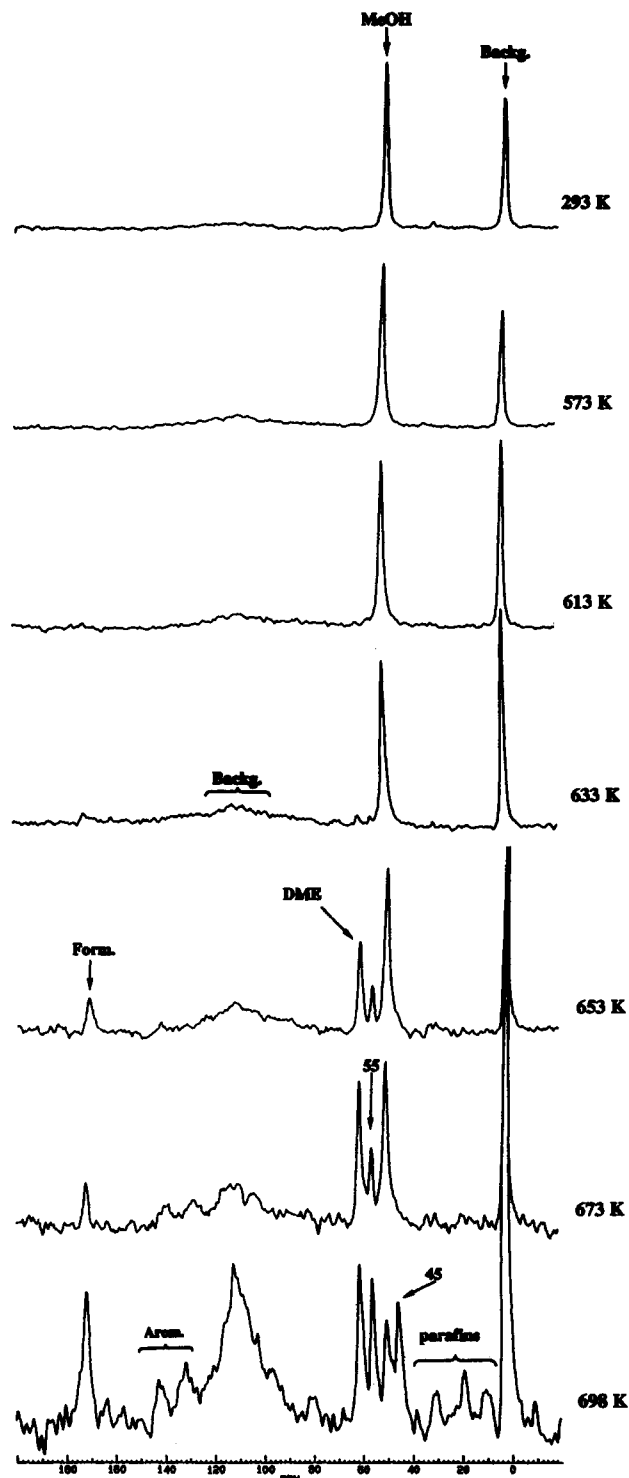

Figure 1. ^{13}C MAS NMR spectra of methanol decomposition on Na-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether; Form, formate; Arom, aromatic carbons).

The main points to notice are that (i) both the Na-X and K-X samples have a high level of exchange and (ii) the Cs-X necessarily has a lower level of exchange owing to the inaccessibility of cation sites within the sodalite cages and double six-membered rings to these large cations.[27,28]

Methanol Decomposition. In order to simplify the steps in the alkylation reaction initially the fate of methanol alone on the catalysts was monitored.

(a) **Methanol on Na-X.** Figure 1 shows the ^{13}C spectra for methanol decomposition over Na-X at a range of temperatures.

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Initially only one resonance is observed at 50 ppm characteristic of adsorbed methanol. Decomposition begins at ca. 653 K with the appearance of signals at 55, 60, and 170 ppm. The resonance at 60 ppm is characteristic of dimethyl ether and indicates some dehydration of the methanol. After pumping on this sample the signal at 60 ppm is removed, indicating that this resonance does not correspond to surface-bound species. The resonance at 55 ppm has a chemical shift which strongly suggests a type of methoxide ion. This resonance is easily removed by pumping which indicates that the species is not strongly bound. Resonances with similar chemical shifts have been observed previously for methyl iodide adsorbed on Na-X.[26] The nature of this species is discussed later. The resonance at 170 ppm is indicative of a formate species. Similar resonances also appear for K-X and Cs-X catalysts at slightly different chemical shifts. An investigation of the formates structure is given later. At higher temperatures a new resonance is observed at 45 ppm and traces of low molecular weight paraffins (C_1–C_4) appearing in the region of –10 to 30 ppm. The resonance at 45 ppm is not easily removed by pumping, which indicates a strong adsorption complex, and the chemical shift is indicative again of a methoxide ion species. Additionally, at high temperatures, a small number of aromatic resonances are observed at ca. 130–143 ppm, which suggests that residual protons are responsible for conversion of methanol to aromatics (methanol-to-gasoline MTG process).

   (b) Methanol on K-X. Figure 2 shows the ^{13}C MAS NMR spectra for the decomposition of methanol over K-X. The decomposition of methanol begins at a temperature ca. 40 K lower than for Na-X, indicating a higher activity for the K-X catalyst. This increase in activity is probably a result of the increase in basicity[2,13] of the K-X over Na-X. Previous reports[2] have shown that the basic strength increases with the increase of the alkali cation radius and the aluminum content. For a zeolite with a given aluminum content, exchange of Na$^+$ with K$^+$ cations results in a large increase of the framework oxygen charge.[2] Introduction of Cs$^+$ cations rather than K$^+$ cations, on the other hand, results in only a slightly higher framework oxygen charge than for K-X. The decomposition reaction (see Figure 2) for K-X starts at ca. 613 K with resonances appearing at 60, 55, and 53 ppm. The resonance at 60 ppm can be assigned to dimethyl ether and the other two resonances to methoxide ions. Again the nature of these ions is discussed later. At higher temperatures the intensity of the line at 60 ppm continues to increase while the intensities of the lines at 53 and 55 ppm remain almost constant. Additionally, at 653 K a resonance at 168 ppm is observed which can be assigned to a formate as well as a small amount of CO at 183 ppm.

   (c) Methanol on Cs-X. Figure 3 shows the ^{13}C MAS NMR spectra for the decomposition of methanol over Cs-X. Decomposition starts at ca. 573 K with the appearance of a small resonance at 60 ppm corresponding to dimethyl ether. The very high activity of this catalyst could result from either the large number of residual protons contained in this sample (Table 1) or the high basicity of Cs-X. However, the strength of the acid sites in zeolite X is very low[26] and therefore they are unlikely to be responsible for the high activity. At higher temperatures the line at 60 ppm dominates the spectra. At 633 K a signal at 165 ppm appears, corresponding to formate. At 653 K a further resonance at 45 ppm appears, corresponding to another type of methoxide ion. The resonance at 45 ppm is not easily removed by pumping—in contrast to the lines at 55 and 53 ppm for Na-X and K-X—suggesting that it corresponds to a strongly bound species. At 653 K a line at 183 ppm also appears which corresponds to CO. At even higher temperatures traces of low molecular weight paraffins are observed in the region from –10 to 35 ppm, including methane at –8 ppm. At the same temperatures the line at 60 ppm is considerably decreased while the lines at 45, 165, and 183 ppm are considerably increased.

   Formate Structure. All the resonances in the region 165–170 ppm are indicative of formate groups. These resonances could
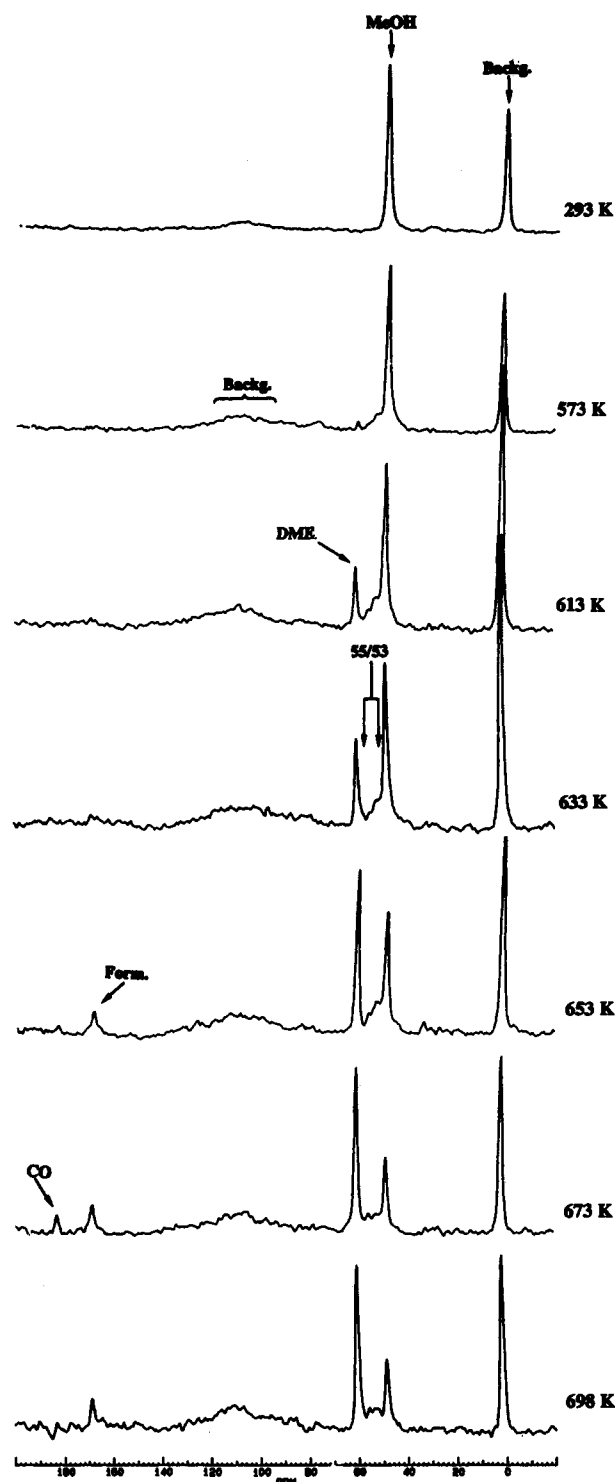

Figure 2. ^{13}C MAS NMR study of methanol decomposition on K-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether; Form, formate).

not be completely eliminated even by extensive pumping on the sample (see Figure 4), which indicates that they are relatively strongly bound. (It should be noted that in Figure 4 comparison is made between a MAS spectrum before pumping and a CPMAS spectrum after pumping. Without CP the signal intensity after pumping is considerably reduced, indicating that pumping does remove species to some extent.) In order to further study the nature of the formates the spectra were recorded either static or with a very low spinning rate. This latter technique yields a spinning side-band pattern, the envelope of which approximately traces the static line shape. This method usually yields spectra with a better signal-to-noise ratio than static spectra. On both Cs-X and K-X the formate resonance appears both narrow and
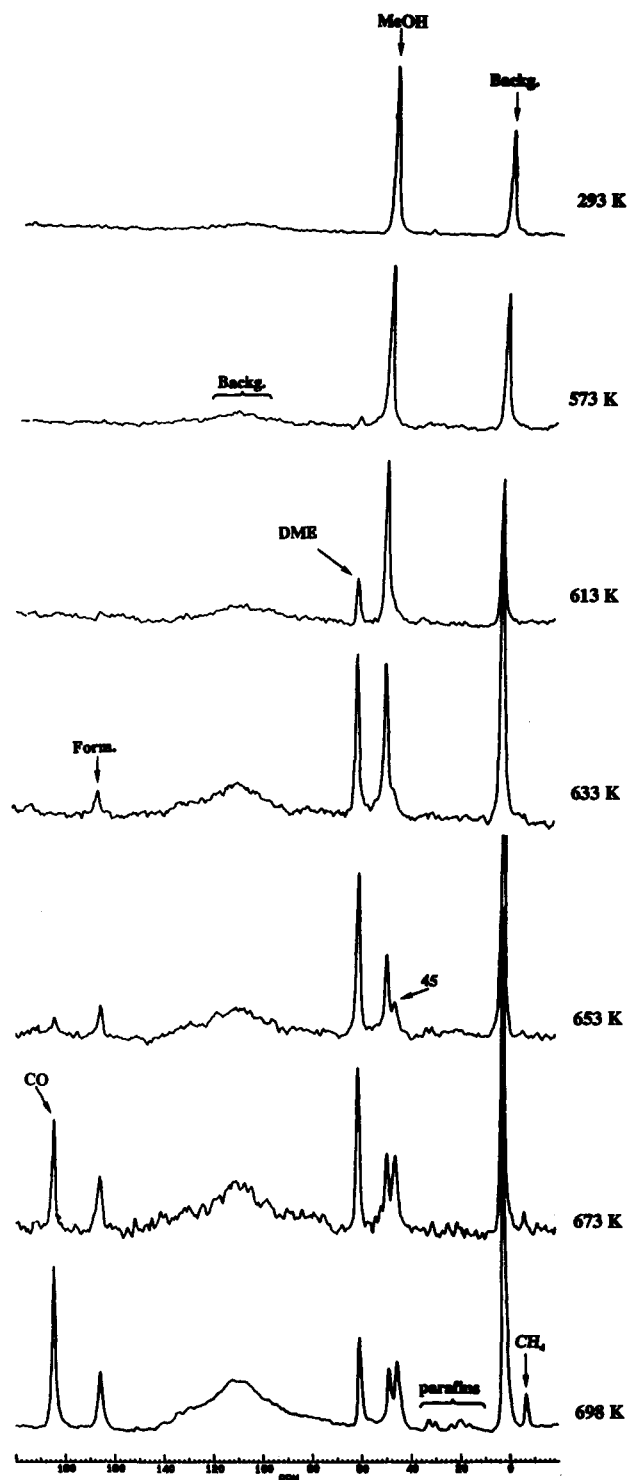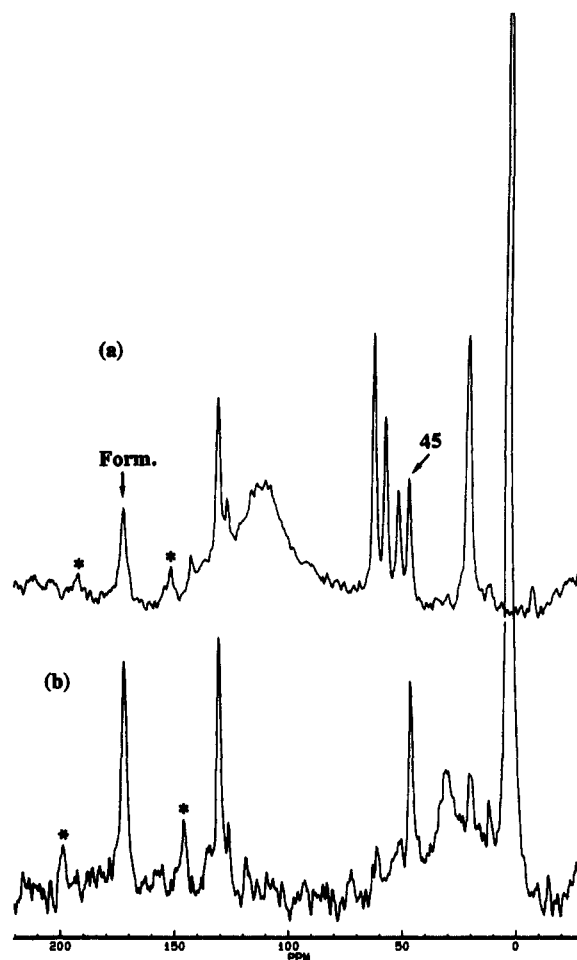
Figure 4. ^{13}C MAS NMR study of the reaction of 3:1 toluene–methanol on Na-X heated up to 673 K (a) before pumping and (b) after pumping recorded with cross polarization. The strongly bound species giving rise to the lines at 45 and ca. 170 ppm appeared in all the spectra recorded after pumping. Asterisks denote spinning sidebands.

Figure 3. ^{13}C MAS NMR study of methanol decomposition on Cs-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether, Form, formate).

symmetric (see Figure 5) whereas on Na-X the signal is considerably broader. This is consistent with two different types of formate structure as already suggested from infrared studies,[29,30] i.e. monodentate attachment on Cs-X and K-X and bidentate attachment on Na-X (also shown in Figure 5). NMR spectra of formates have also been observed upon adsorption of formic acid on acidic Y-type zeolites.[31] The same formate structures

are also suggested by recent MAS NMR studies[32] of methanol decomposition on Cu/ZnO/Al$_2$O$_3$.

Alkylation Reaction of Toluene with Methanol. At low temperatures the ^{13}C spectra on both Na-X and K-X appears very similar to those in the absence of toluene. This indicates that there is no strong interaction between the methanol and the toluene in these catalysts. However, in the case of Cs-X (Figure 6), an additional broad signal is observed at room temperature shifted ca. 0.5 ppm downfield from the methanol resonance. This signal results either from a strong interaction of the methanol with the toluene or the toluene modifying the surface adsorption site for methanol. This additional signal is also amenable to cross polarization, unlike the narrow methanol resonance, again indicating the rigidity of the complex. At 573 K this line is reduced in intensity; however, it can still be observed using cross polarization. At this temperature it exhibits a number of spinning site bands indicating either a further restriction of the mobility of this species or a dipolar interaction with a quadrupolar nucleus such as cesium.

(a) **Methanol and Toluene on Na-X.** Figures 7 shows the ^{13}C MAS NMR spectra of the reaction of toluene with methanol on Na-X. Over this catalyst the ring alkylation and the xylenes formation dominates. The lines at 45, 55, 60, and 170 ppm appear in these spectra as well. Their assignment is the same as in the case of methanol decomposition. At 673 K these four lines are observed in the spectrum along with a signal at 19 ppm due to xylene formation. At 698 K the line at 45 ppm is still present

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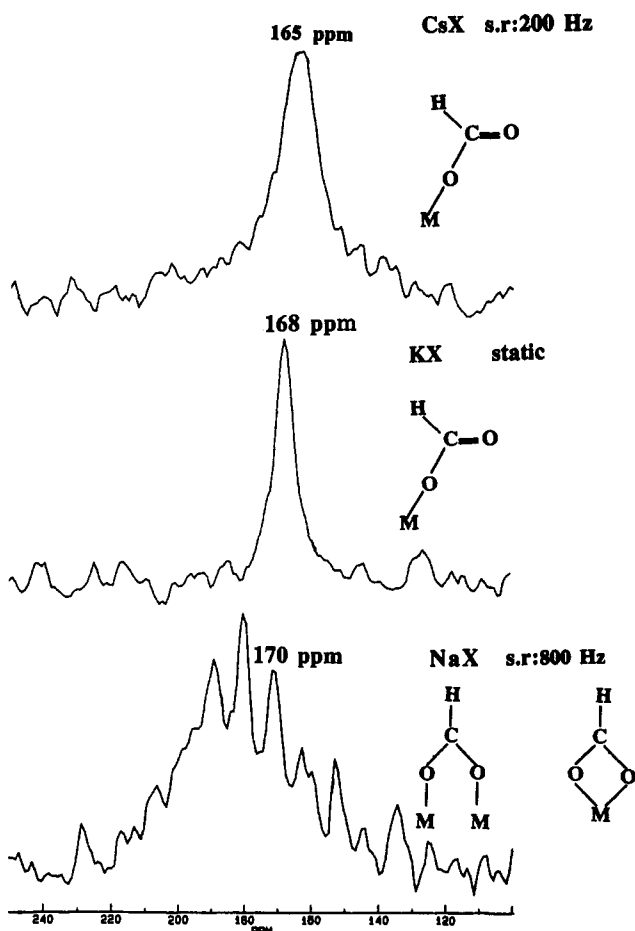
Figure 5. ^{13}C CP MAS NMR spectra of the formates region (a, top) on Cs-X with a slow spinning rate (b, middle), on K-X static, and (c, bottom) on Na-X with a slow spinning rate.

in this spectrum, while the lines at 55, 60, and 170 ppm have decreased approximately to zero. At 723 K the reaction is complete. In this spectrum we only observe a small amount of the formate (170 ppm), ring carbons from all aromatic species (125–140 ppm), xylenes (19 ppm), a small amount of ethylbenzene (15 ppm), and methane (–10 ppm). Figure 8 gives a graphical representation of the amount of products and surface species present at different stages during the reaction. No attempt was made to quantify the aromatic region because the resolution and intensity (^{13}C not enriched) is insufficient.

(b) Methanol and Toluene on K-X. Figure 9 shows the ^{13}C MAS NMR spectra of the reaction of toluene with methanol on K-X. Over this catalyst the side-chain alkylation starts competing with the ring alkylation. At 633 K the lines at 53, 55, and 60 ppm appear and are assigned as above. At 673 K a resonance at 183 ppm appears in the spectrum and is assigned to carbon monoxide. The most important catalytic steps take place in the region 673–698 K. In this temperature region the lines at 60, 55, and 53 ppm are considerably decreased while the ethylbenzene (15 ppm), xylenes (19 ppm), and CO (183 ppm) lines are enhanced dramatically. At the same time, the line at 45 ppm appears with some low molecular weight paraffins (–10 to 30 ppm). The line at 45 ppm is assigned as above. In addition a very broad line is observed at 168 ppm which is assigned to formate. This line is considerably broader here than in the spectrum for methanol on K-X alone. At 723 K the lines at 45, 55, and 60 ppm are no longer present and there is a small increase in the intensity of the ethylbenzene line. Figure 10 shows a graphical representation of this reaction.

(c) Methanol and Toluene on Cs-X. Figure 11 shows the ^{13}C MAS NMR spectra of the reaction of toluene with methanol on Cs-X. Over this catalyst no ring alkylation was observed. On
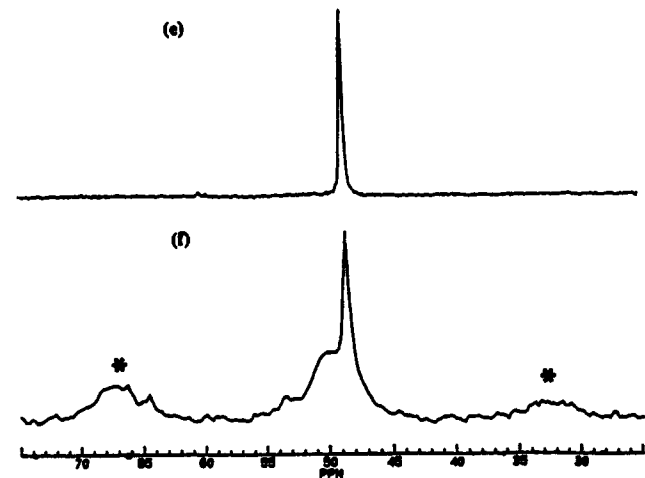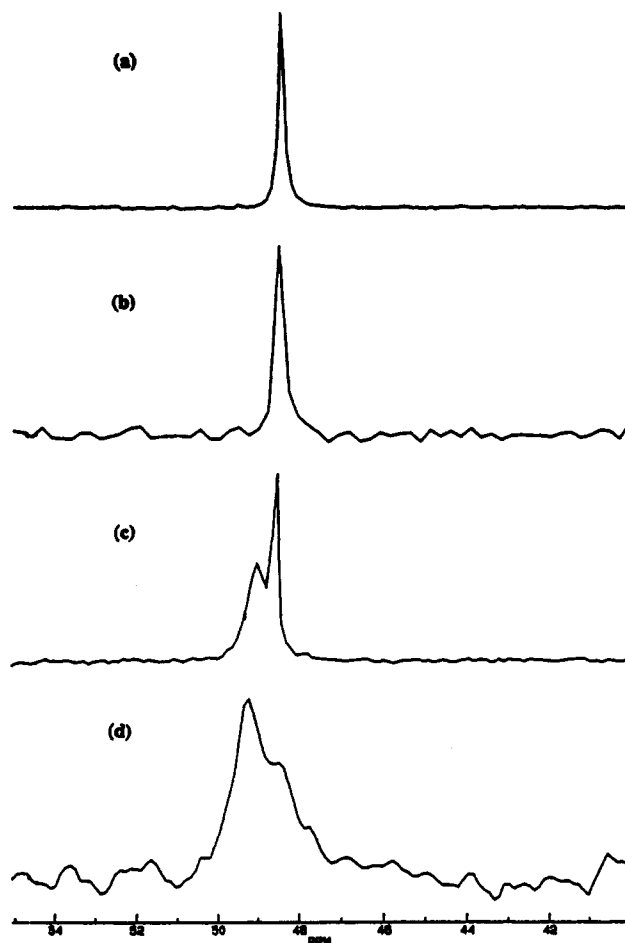

Figure 6. ^{13}C MAS NMR spectra of the toluene–methanol interaction on Cs-X: (a) ^{13}C MAS NMR of methanol at room temperature; (b) ^{13}C CP MAS NMR of methanol at room temperature; (c) ^{13}C MAS NMR of 3:1 toluene–methanol at room temperature; (d) ^{13}C CP MAS NMR of 3:1 toluene–methanol at room temperature; (e) ^{13}C MAS NMR of 3:1 toluene–methanol heated up to 573 K; (f) ^{13}C CP MAS NMR of 3:1 toluene–methanol heated up to 573 K. Asterisks denote spinning sidebands. In this series of spectra 15-Hz line broadening has been applied only in the cases of (d) and (f).

this catalyst the main catalytic events take place between 633 and 653 K. In this temperature region, styrene is formed giving rise to a line at 115 ppm and a small amount of ethylbenzene is observed at 16 ppm. Meanwhile the resonance at 165 ppm appears while the line at 60 ppm keeps increasing (both assigned as above). As with K-X the formate line is very broad. At 673 K the
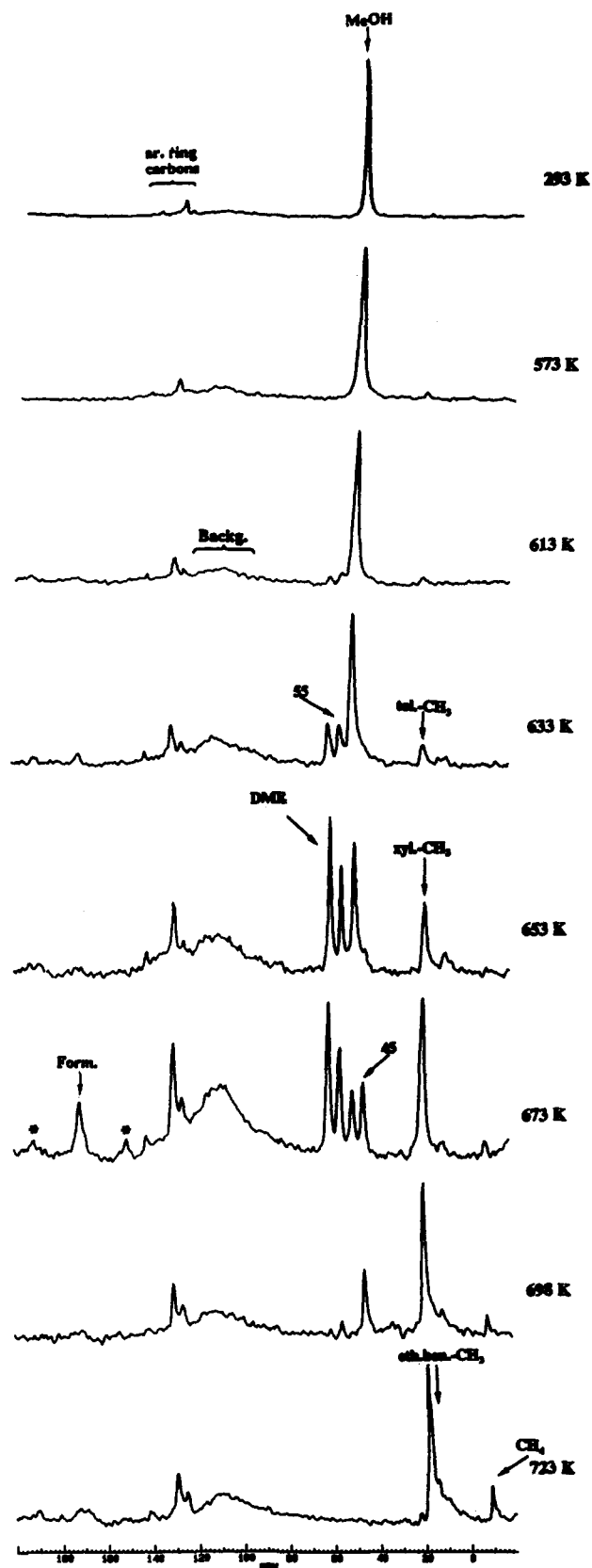
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Figure 7. ^{13}C MAS NMR study of the reaction of 3:1 toluene–methanol on Na-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether; Form, formate; xyl-CH₃, xylene methyl resonance; tol-CH₃, toluene methyl resonance; eth ben-CH₃, ethylbenzene methyl resonance; ar, aromatic). Asterisks denote spinning sidebands.

ethylbenzene line is enhanced markedly and is associated with the appearance of the line at 45 ppm. The same spectrum shows the presence of CO in a very small amount. In the last two spectra of this series ethylbenzene formation dominates while the
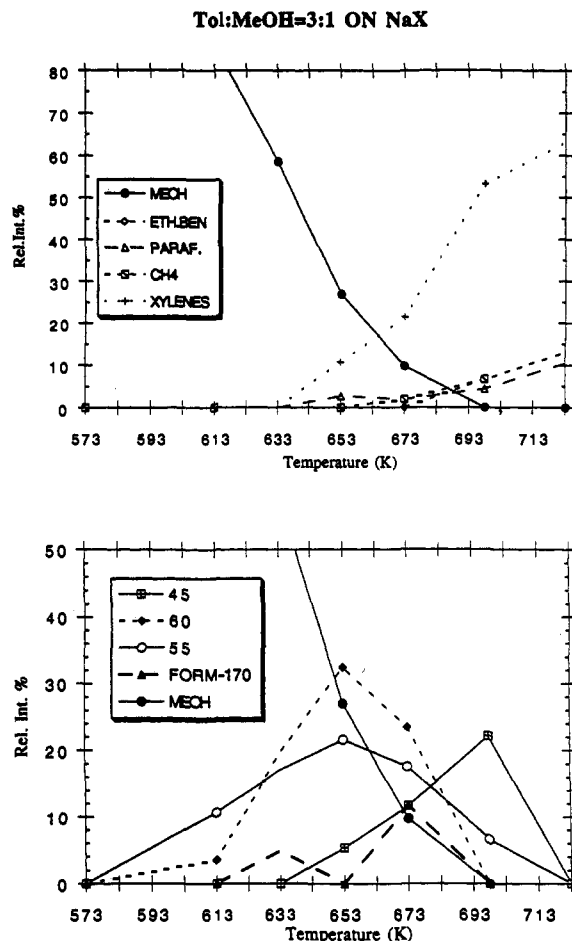
Figure 8. A graphical representation of the intermediate and final product distribution vs temperature during the reaction of 3:1 toluene–methanol on Na-X.

styrene line decreases to zero intensity. At the same temperatures the lines at 45 and 60 ppm decrease to zero while the CO line rises noticeably. Figure 12 shows a graphical representation of this reaction. It should be noted that the $-^{13}CH_{2}-$ group in ethylbenzene is not observed because it originates from unenriched toluene and is therefore only 1% of the concentration of the $^{13}CH_3-$ group which originates from enriched methanol. A similar situation accounts for the absence of signals for $-CH=$ groups in styrene.

Discussion

Selectivity for Side-Chain Alkylation. The results of this work confirm that the selectivity for side-chain alkylation increases with the increase of the alkali cation size (Cs > K > Na). Over Na-X only traces of side-chain alkylation were observed with the formation of xylenes dominating. The selectivity of side-chain alkylation was found to increase considerably in the case of K-X, up to approximately 60%. Over Cs-X only side-chain alkylation was observed. The methanol decomposition experiments showed that the activity for decomposition also increased in the series Cs-X > K-X > Na-X. The more active the catalyst for methanol decomposition the more selective for side-chain alkylation.

Nature of Surface Species. During the course of the alkylation reaction a number of resonances occur which cannot be assigned to species in the product stream. These must therefore correspond to species which are formed inside the zeolite catalyst at the active sites and exist as stable surface species. Further, all these species originate from the methanol component and not the toluene. Two questions must be answered: (i) what is the nature of these species; (ii) are these species involved in important catalytic reaction steps?
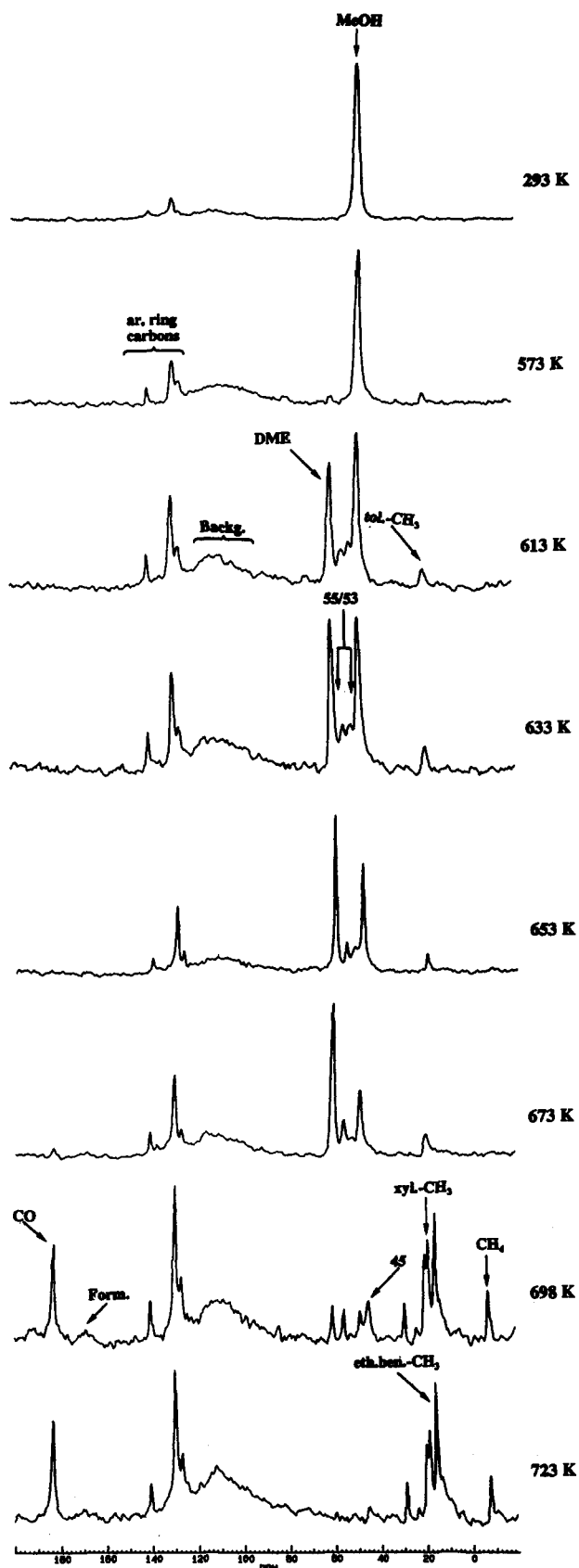
Figure 9. ^{13}C MAS NMR study of the reaction of 3:1 toluene–methanol on K-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether; Form, formate; xyl-CH$_3$, xylene methyl resonance; tol-CH$_3$, toluene methyl resonance; eth ben-CH$_3$, ethylbenzene methyl resonance; ar, aromatic).

Formate Resonance. The nature of the formate species has already been addressed within the Results section. Clearly there is a fundamental difference between the type of formate structure
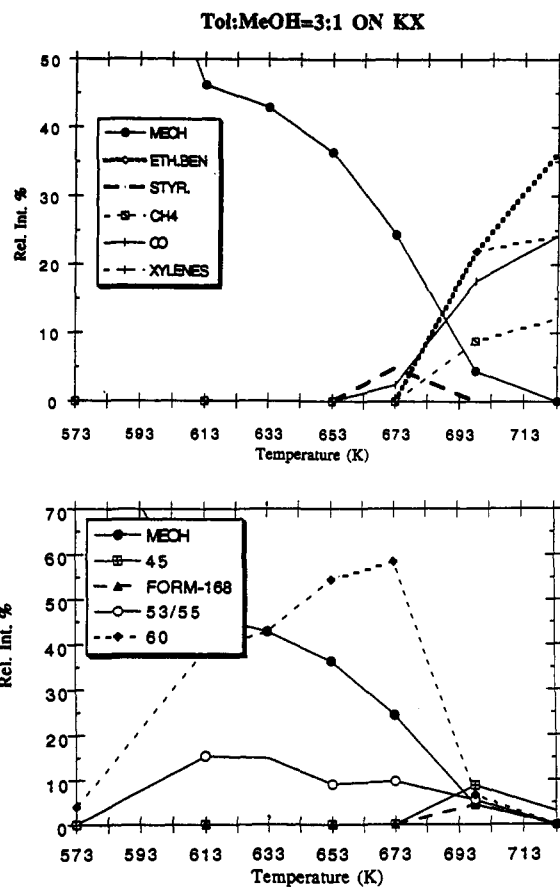

Figure 10. A graphical representation of the intermediate and final products distribution vs temperature during the reaction of 3:1 toluene–methanol on K-X.

on Na-X, with a bidentate attachment, and on K-X and Cs-X, with a monodentate attachment. With reference to Figures 3 and 11, where methanol and toluene/methanol are adsorbed on Cs-X respectively, there is a clear association between the appearance of the formate resonance and the appearance of this methoxide ion resonance at 45 ppm. Indeed, there is almost a 1:1 correspondence between the intensity of the formate resonance and the methoxide ion resonances on Cs-X. The formation of the formate species can be considered to originate from a methanol complex thus:

(1)
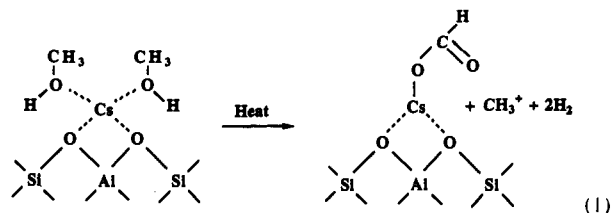
The fate of the methyl carbocation thus formed is discussed later. All the formate species are very strongly bound to the zeolite surface, indicated by the difficulty in removing these species by pumping. This strong binding makes them less likely to be the alkylating agent.

Methoxide Ions. The resonances at 45, 55, and 53 ppm can all be assigned to types of simple methoxide ions based on the following: (i) the chemical shift; (ii) the resonances appearing independently of each other indicating that they do not come from the same molecule, i.e. each species contains only one magnetically inequivalent carbon; (iii) the resonances appearing independently of the formate resonance in some spectra indicating again that they are not from the same molecule as the formate resonance.
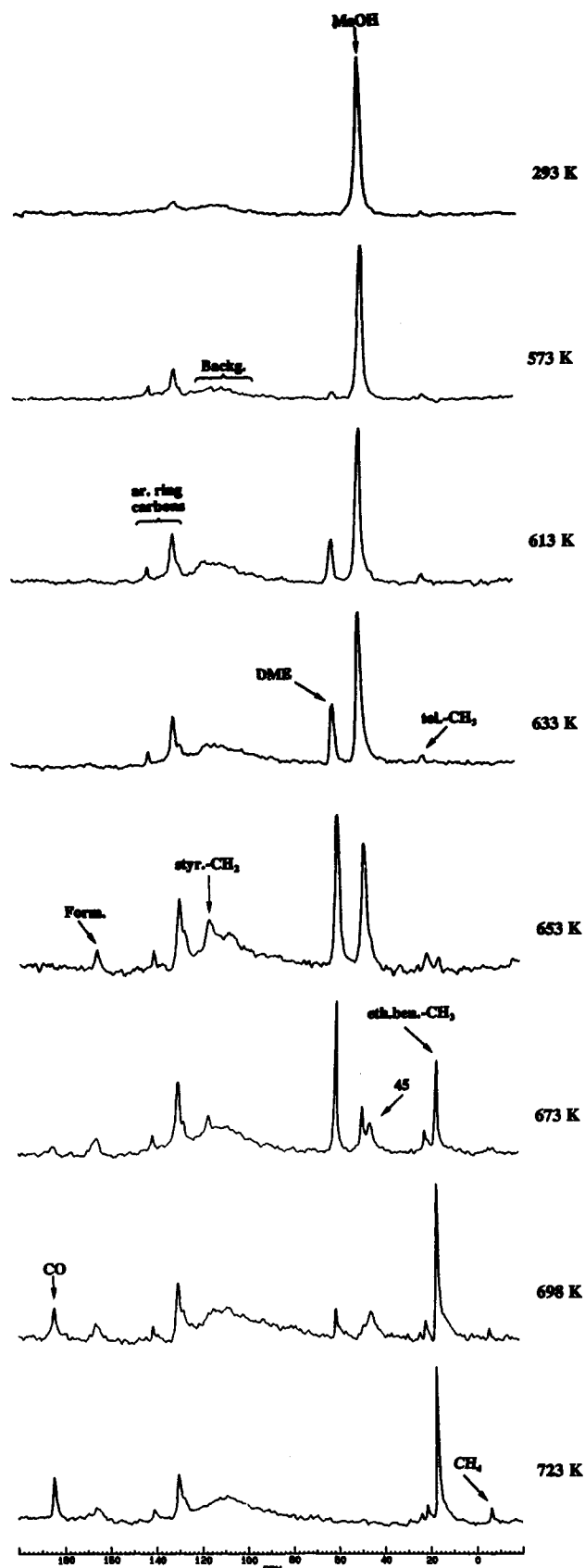
Alkylation of Toluene with Methanol

J. Am. Chem. Soc., Vol. 116, No. 13, 1994 5781
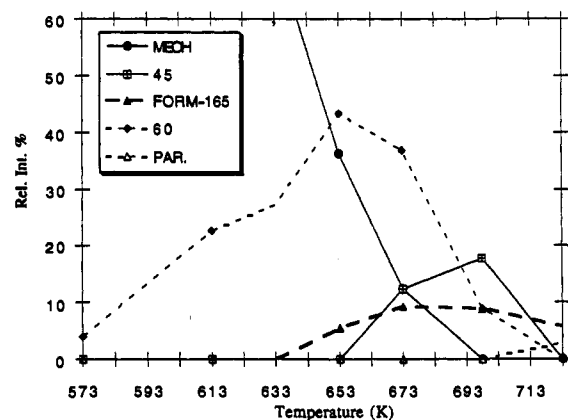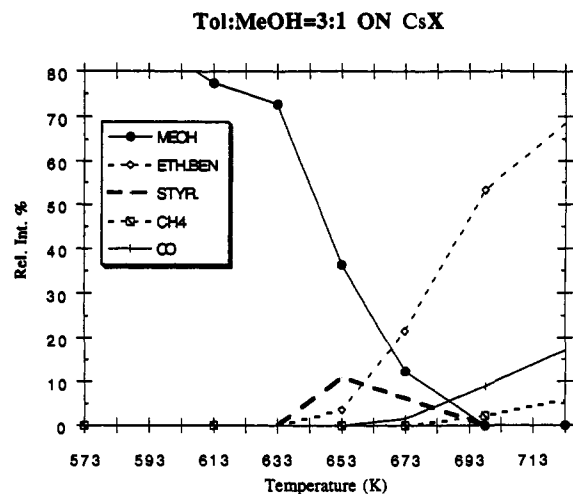
Tol:MeOH=3:1 ON CsX

Figure 12. A graphical representation of the intermediate and final products distribution vs temperature during the reaction of 3:1 toluene–methanol on Cs-X.

Figure 11. ^{13}C MAS NMR study of the reaction of 3:1 toluene–methanol on Cs-X (MeOH, methanol; Backg, background signal; DME, dimethyl ether; Form, formate; tol-CH$_3$, toluene methyl resonance; eth ben-CH$_3$, ethylbenzene methyl resonance; ar, aromatic; styr-CH$_2$, styrene methylene resonance). In the spectrum recorded at room temperature we cannot see the additional broad line resulting from the toluene–methanol interaction as in Figure 6c since 100-Hz line broadening has been applied in all these spectra in order to improve the signal-to-noise ratio.

The species corresponding to the resonance at 45 ppm is much more strongly bound than the species corresponding to the other two resonances—this is ascertained by trying to remove the species by pumping. This indicates that the nature of the species corresponding to the line at 45 ppm is substantially different from the other two resonances. Also the chemical shift of this species is independent of the nature of the alkali metal and therefore is probably associated only with the zeolite framework. The most likely explanation for the line at 45 ppm is a surface bound methoxy group on a bridging zeolitic oxygen as shown below
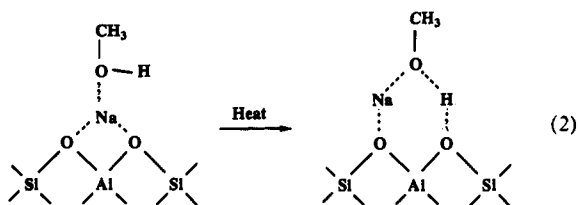
Complex I
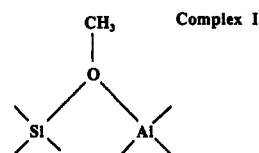
Such a species must be formed by alkylation of the zeolite by methyl carbocations formed via reaction 1. It would be strongly adsorbed and difficult to remove by pumping. Murray et al.[26] assigned a resonance at 58 ppm to surface bound methoxy groups in alkali-metal exchanged zeolite X based on experiments with adsorbed methyl halides. It is difficult to compare their assignments with this work as the state of the catalyst is quite different. On our catalysts the alkali metal cation is probably complexed as a formate as shown by reaction 1 above. In the work of Murray et al. they must form some metal halide which might interact differently with the surface bound methoxide.

The resonances at 53 and 55 ppm are easily removed by pumping and therefore must represent weakly adsorbed species. We suggest
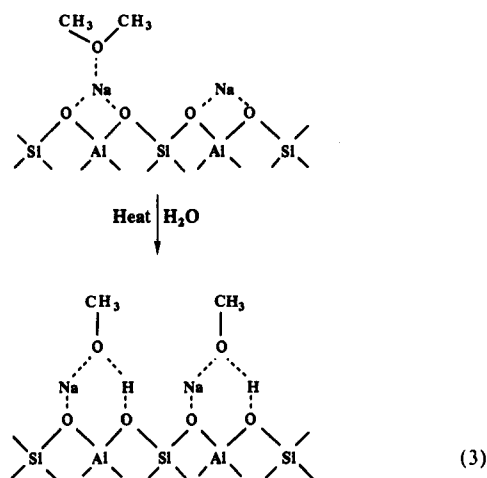
that these species are protonated metal methoxy species (**II**) as shown below.

Complex II
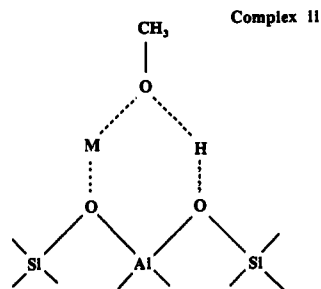
Such a type II species could be formed either from methanol requiring displacement of the metal cation from its original crystallographic siting

$$(2)$$

or from dimethyl ether via the following

$$(3)$$

The chemical shift for type II species is also consistent with that of solid sodium methoxide which has a value of 55 ppm. The lines at 55 and 53 ppm will be complexes with sodium and potassium cations, respectively. There seems to be a correlation between the degree of the type II complex formation and the cation size. Over Na-X this complex is formed in abundance (observed at 55 ppm in Figures 1 and 7), while on K-X the type II complex involving the K cations (observed at 53 ppm in Figures 2 and 9) is hardly formed. Finally, on Cs-X this complex is not formed at all. This shows that the larger the cation size, the less stable the type II complex. The response of our signals at both 53 and 55 ppm in terms of both line width and spinning side bands is quite different from the resonance at 58 ppm reported previously[26] for surface bound methoxy groups. The adsorbed species II would be easily removed as methanol by pumping, owing to the expected weak interaction between the proton and the framework oxygen in zeolite X.

Reaction Mechanism. The accepted mechanism for side-chain alkylation suggests that formaldehyde is the alkylating agent. In our experiments we have never observed this molecule. However, formaldehyde is very unstable and can decompose to CO and H_2 and therefore the presence of CO is a telltale sign that formaldehyde might have formed. In our experiments the presence of CO is associated with the side-chain alkylation (on

K-X and Cs-X). This suggests that formaldehyde could be formed on these catalysts, some of which immediately attacks the toluene methyl group while a proportion decomposes to form CO and H_2.

It has been suggested[33] that formaldehyde can be formed from the conversion of a Cs^+ methanol complex. On Cs-X we never observe a complex of type **II** exhibiting a line at ca. 55 ppm, suggesting that methanol forms only a simple interaction with Cs^+ through the oxygen of the hydroxyl group. There is no associated interaction with the zeolite. We suggest that this is due to the large size of the Cs^+ cation which prevents reactions similar to those in eqs 2 and 3 occurring. On Cs-X two routes could be followed: either formaldehyde is formed by the following dehydrogenation process

$$(4)$$
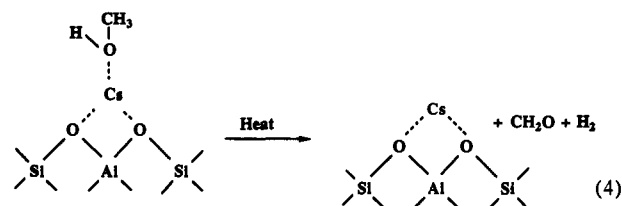
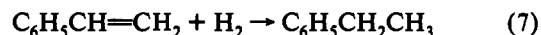or formate and methyl carbocations are formed via reaction 1.

The formaldehyde formed by reaction 4 will either decompose to CO and H_2

$$CH_2O \rightarrow CO + H_2 \qquad (5)$$
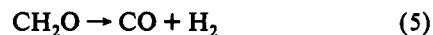
or attack the toluene at the side chain

$$C_6H_5CH_3 + CH_2O \rightarrow C_6H_5CH=CH_2 + H_2 \qquad (6)$$

The styrene produced will subsequently be hydrogenated, using hydrogen from reactions 1, 4, and 5 to give ethylbenzene

$$C_6H_5CH=CH_2 + H_2 \rightarrow C_6H_5CH_2CH_3 \qquad (7)$$

Important Additional Role of Cs-X in Side-Chain Alkylation. Our results also suggest that the Cs-X plays another crucial role in preventing ring alkylation, and consequently promoting side-chain alkylation, through the formation of stable surface bound methoxy groups. The presence of surface bound methoxy groups, evidenced by the resonance at 45 ppm, must have been formed by the presence of methyl carbocations


$$(8)$$
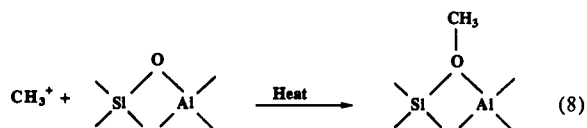
It has already been shown that the methyl carbocations are formed by reaction 1 and are therefore also associated with the formation of surface formates—as observed. Usually the preferable reaction of toluene in the presence of methyl carbocations is for attack at the ring to form xylenes. This does not happen

(33) Archier, D.; Coudurier, G.; Naccache, C. *Proceedings of the 9th International Zeolite Conference*, Montreal, 1992, R. von Ballmoos et al., Eds.; Butterworth-Heinemann: London, 1993; Vol. II, 525.

on Cs-X because of the preference for reaction 8. Therefore the Cs-X zeolite is acting as a gettering agent for methyl carbocations to form stable surface bound methoxy groups. The stability of these groups is presumably a function of the electronegativity of the zeolite which is greatest in the case of Cs-X.

In the case of Na-X mainly ring alkylation is observed and no CO is produced. Both these facts indicate that formaldehyde is not produced via routes analogous to reaction 4. On Na-X there is a large concentration of species of type II which, as Na-X is particularly efficient for ring alkylation, probably decompose to methyl carbocations as follows


$$(9)$$
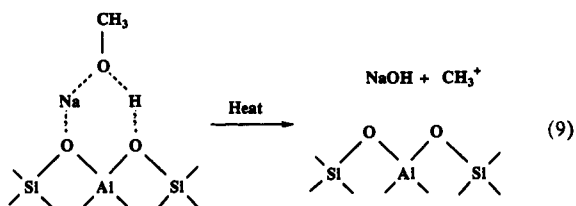
The methyl carbocation formed via reaction 9 can then either attack the ring of toluene

$$C_6H_5CH_3 + CH_3^+ \rightarrow C_6H_4(CH_3)_2 + H^+ \qquad (10)$$

or become stabilized on the zeolite as a surface-bound methoxy via reaction 8. Owing to the lower electronegativity of Na-X over Cs-X, reaction 10 is favored over reaction 8 allowing ring alkylation to proceed freely. Also, on Na-X and K-X there are two possible sources of methyl carbocations, either reaction 1 or 9, whereas on Cs-X there is only one, reaction 1. Consequently on Na-X and K-X there are more methyl carbocations available for ring alkylation. Further evidence for the different competing routes to methyl carbocation formation comes from the relative intensities of species. On Cs-X, as stated previously, the formate resonance and the line at 45 ppm come in a 1:1 ratio at all temperatures corresponding only to reaction 1. However, on Na-X and K-X, where there are competing routes to methyl carbocation formation, each potentially producing the resonance at 45 ppm but also each involved in the ring alkylation step, there is no strict 1:1 correlation between the formate resonance and that at 45 ppm.

The methyl carbocation formed in reaction 1 or 9 can also attack methanol which would result in the following reaction producing more dimethyl ether.


$$(11)$$
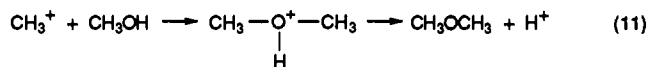
This is an important reaction at low temperatures on Na-X and K-X where CH_3^+ species are formed (evidenced by formation of

formates), but they do not produce either surface methoxy groups (line at 45 ppm) or xylene products.

It is important also to consider the fate of dimethyl ether over these catalysts as it is always present in abundance prior to product formation. The presence of dimethyl ether has been previously reported[12] to be associated with ring alkylation. To some extent, the results of the present work agree with this since over Na-X and K-X dimethyl ether can form complex II via reaction 3 and then produce methyl carbocations via reaction 9. On Cs-X, however, this does not occur as complex II is never formed. An alternative route from dimethyl ether to formaldehyde over Cs-X can be considered as an additional route to side-chain alkylation.

$$CH_3OCH_3 + H_2O + Cs^+Z^- \rightarrow 2CH_2O + 2H_2 + Cs^+Z^- \qquad (12)$$
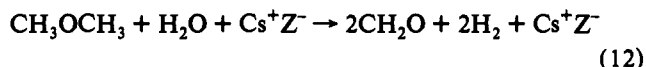
Finally, it is of interest to consider whether any of the surface methoxy species observed are directly involved in the side-chain alkylation process. If this is the case then the alkylating agent would be CH_3^+. Consequently, in order for this carbocation to attack the side chain rather than the ring it would be first necessary to propose the existence of a phenylcarbanion such as C_6H_5-$CH_2^-Cs^+$. Direct alkylation by CH_3^+ would then directly produce ethylbenzene

$$C_6H_5CH_2^-Cs^+ + CH_3^+ \rightarrow C_6H_5CH_2CH_3 + Cs^+ \qquad (13)$$
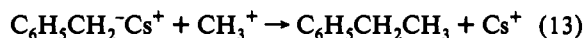
Although reaction 13 is feasible, it cannot explain the formation of styrene which is always observed. Consequently, it cannot be the only path for side-chain alkylation and we suggest that it is less likely than the route via formaldehyde.

Conclusion

Solid-state ^{13}C NMR measurements on the alkylation of toluene with methanol have been used to successfully identify both reaction products and surface-bound species. These surface-bound species give important clues as to the mechanism of both the side-chain alkylation and the ring alkylation. For side-chain alkylation it is concluded that formaldehyde acts as the alkylating reagent. However, the zeolite also plays an important role gettering highly reactive methyl carbocations as stable surface-bound methoxy species. The most basic Cs-X is particularly good in this respect thereby preventing any ring alkylation. The Cs^+ cations are also important for promoting the formation of formaldehyde which is formed to a lesser extent on K-X and not at all on Na-X. On Na-X ring alkylation occurs by attack of toluene by methyl carbocations. The methyl cations are formed either by the decomposition of bound protonated sodium methoxy species or through the production of formates. Consequently, many more methyl carbocations are formed on Na-X than Cs-X. Coupled with this the Na-X is far less electronegative than Cs-X and does not getter these carbocations as efficiently. On all catalysts surface-bound metal formate species are observed, but these act essentially as spectators in the reaction.