JOURNAL OF CATALYSIS **168,** 442–449 (1997)
ARTICLE NO. CA971685

Selective Alkylation of Toluene over Basic Zeolites: An *in Situ* Infrared Spectroscopic Investigation

A. E. Palomares, G. Eder-Mirth, and J. A. Lercher

Department of Chemical Technology, University of Twente, P.O. Box 217,7500 AE-Enschede, The Netherlands

Received October 16, 1996; revised February 12, 1997; accepted February 12, 1997

***In situ* infrared spectroscopy was used to study the sorption and reaction of toluene and methanol over various alkali exchanged X zeolites. The size of the metal cations controls the preference of sorbing methanol or toluene. The smaller the cation, the higher the preference for methanol is. A balanced sorption stoichiometry of the reactants, the intermediate conversion of methanol into formaldehyde and the strong polarization of the methyl group of toluene are critical to catalyze side chain alkylation of toluene. These requirements are best met with very basic zeolites such as the Cs-X and Rb-X.** © **1997 Academic Press**

---

1. INTRODUCTION

The side-chain alkylation of toluene with methanol over basic materials, can produce styrene and ethylbenzene (1, 2). The process has been claimed to be economically attractive (3) offering the advantage of lower raw material cost compared with the traditional process. This may also be the reason why this reaction is one of the few well-studied cases of base catalysis. As early as 1957 (4) it was shown that basic catalysts could be used to selectively add olefins to the alkyl aromatic side chain, while acidic catalysts induce olefin addition to the aromatic ring. Similarly, alkylation of toluene with methanol over acidic zeolites leads to alkylation on the ring (5–7), while basic zeolites are known to catalyze side chain alkylation (8–10). Whereas the base catalysts applicable for this reaction are not confined to zeolites (MgO and CaO were successfully used (11)), recent studies indicate that alkali metal (hydr)oxides supported in the zeolite pores might be indispensable to catalyze the reaction (12).

The role of the overall acid–base properties of zeolite catalysts for the selectivity in the alkylation of aromatic molecules is well compiled by Giordano *et al.* (13). It is generally believed that dehydrogenation of methanol to formaldehyde (which only occurs over basic catalysts) is the most important chemical step (9, 14), but other factors such as the electrostatic field experienced by the aromatic nucleus, also seem to determine the selectivity of the reaction (15). Moreover, the extent of the additional involvement of acid sites in the side chain alkylation of alkylbenzenes (12, 16–20) is still debated.

The purpose of the present contribution is, thus, to compare the surface chemistry on the working catalysts during toluene alkylation and to relate it with the catalytic activity and selectivity of various alkali exchanged faujasites. Parallel *in situ* i.r. spectroscopic and kinetic measurements are used to show how chemisorption and stabilization of the reactants at the surface relate to the catalytic properties of zeolites.

2. EXPERIMENTAL

2.1. *Materials*

Alkali cations (Cs^+, Rb^+, K^+, and Na^+) exchanged zeolites X were prepared from a commercial Na-X zeolite, obtained from Fluka. The parent zeolite was exchanged three times at 353 K, during 22 h with a 0.025 *M* solution of potassium oxalate, rubidium acetate, or cesium acetate (solid/liquid ratio $= 15\ g \cdot l^{-1}$). To avoid the formation of acid sites which could catalyze ring alkylation, samples were not rinsed with water after the last exchange. The chemical composition of the catalysts was analyzed by atomic absorption spectroscopy and the results are compiled in Table 1. The values indicate that some silica is removed by the ion exchange procedure and that the presence of trace amounts of oxide phase containing alkali cations cannot be excluded.

2.2. *Sorption and Coadsorption Experiments*

I.r. spectroscopy was the primary means used to characterize the sorbed species. The zeolite powder was pressed into self-supporting wafers and analyzed *in situ* during all treatments by transmission absorption i.r. spectroscopy using a Bruker IFS88 FTIR spectrometer (4 cm^{-1} spectral resolution). For sorption experiments, a stainless steel cell with i.r. transparent windows that could be evacuated to pressures below 10^{-6} mbar[1] was used (for details see Ref. (21)). The activated sample wafer was contacted with the appropriate pressure of the adsorptive at constant temperature

---

[1] 1 mbar $= 10^2\ N/m^2$.

0021-9517/97 $25.00

TABLE 1

Chemical Composition of Alkali Exchanged X-Zeolites [% mol]

Catalyst	SiO_2	Al_2O_3	Na_2O	K_2O	Rb_2O	Cs_2O
Na-X	56.2	21.9	21.9	—	—	—
K-X	50.4	20.8	5.9	22.9	—	—
Rb-X	54.6	21.6	9.3	—	14.5	—
Cs-X	52.4	20.9	10.0	—	—	16.7

($T = 308$ K) until adsorption–desorption equilibrium was achieved (monitored by time resolved i.r. spectroscopy). For the coadsorption experiments, the catalyst was first equilibrated with one reactant. Subsequently, the loaded zeolite was exposed to 5×10^{-3} mbar of the second reactant until the adsorption/desorption equilibrium was reached (while keeping the partial pressure, 5×10^{-3} mbar, of the first reactant constant). Then, the sample was evacuated for 1 h at room temperature. The remaining sorbed molecules were removed by temperature programmed desorption (up to 773 K) while analyzing the desorbing species by mass spectroscopy.

The surface coverage was quantified by calibration with gravimetric measurements under conditions identical to the i.r. spectroscopic experiments (308 K and 5×10^{-3} mbar).

2.3. Reaction Studies

For the *in situ* reaction studies, an i.r. cell with the characteristics of a well-stirred continuously operating tank reactor (volume = 1.5 cm^3) equipped with 1/16″ gas in- and outlet tubing and CaF_2 windows was used (22). To characterize the sorbed species in the zeolite pores during catalytic reaction, i.r. spectra were recorded time resolved, as the activated zeolite was contacted with a He stream (3.5 ml/min) containing the reactants (toluene/methanol = 45/15 mbar). Simultaneously, samples of the effluent gas stream were collected in sample loops of a multiport-valve and subsequently analyzed by gas chromatography (HP5890 II, capillary column DBWAX, 30 m, FID, He as carrier gas).

3. RESULTS

3.1. Adsorption Studies

The i.r. spectra of methanol sorbed on the different zeolites are shown in Fig. 1. The maxima of the most prominent bands were observed at 3216–3336 (stretching vibration bands of the hydrogen bonded OH group of methanol), 2839–2820, 2956–2941 (C−H stretching vibration bands) and 1450–1475 cm^{-1} (C−H deformation vibration bands). As can be seen in Table 2, the wavenumbers of the OH stretching vibration bands were found to be the highest for methanol sorbed on Na-X (3336 cm^{-1}) and progressively decreased to the values of methanol sorbed on Cs-X and Rb-X (3244 and 3216 cm^{-1}). A similar trend was observed with the absorption maxima of the CH stretching vibration bands that varied from 2839 (symmetric stretching mode) and 2956 cm^{-1} (asymmetric stretching mode) for methanol sorbed on Na-X, to 2820–2825 (symmetric stretching mode) and 2941–2942 cm^{-1} (asymmetric stretching mode) for methanol sorbed on Cs-X and Rb-X. The t.p.d of methanol from the various zeolites are shown in Fig. 2. It can be observed that the temperature of the desorption maximum of methanol decreased from Na-X (393 K) to Cs-X, where methanol was rather weakly adsorbed (and could be removed by evacuation at room temperature). Note that this is reflected in the decreasing amount of methanol desorbing.

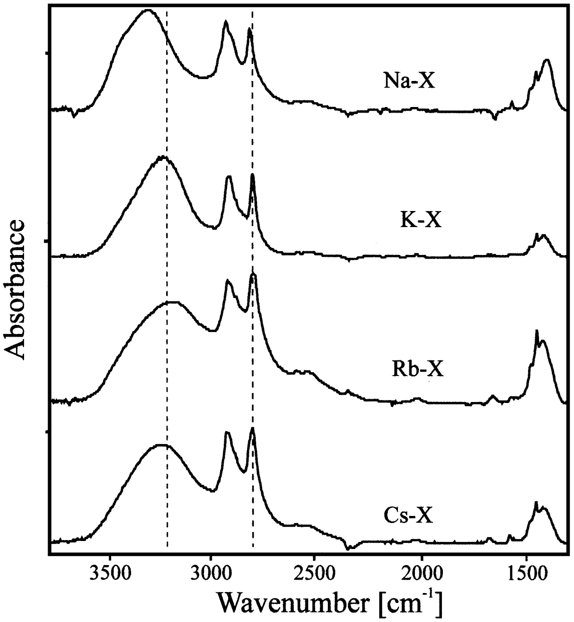


FIG. 1. Difference i.r. spectra of methanol sorbed on alkali exchanged X zeolites ($p = 5 \cdot 10^{-3}$ mbar, $T = 308$ K).

The i.r. spectra of toluene adsorbed on the various zeolites showed only little differences in the absorption maximum and the intensities of the ring vibrations (1598, 1494, and 1465 cm^{-1}), but (see Table 3) the wavenumbers of the C−H stretching vibrations bands of the aromatic ring (3055–3048 and 3024–3021 cm^{-1}) and the methyl group

TABLE 2

I.r. Bands of Methanol Sorbed on Alkali Exchanged X Zeolites

Sample	$\nu_{O\text{−}H}$ [cm^{-1}]	$\nu_{C\text{−}H\ \mathrm{methyl}}$ [cm^{-1}]
Na-X	3336	2839, 2956
K-X	3258	2825, 2943
Rb-X	3216	2825, 2942
Cs-X	3244	2820, 2941

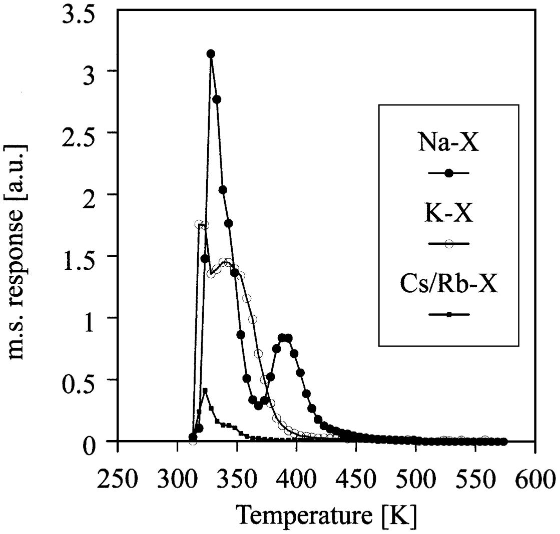


FIG. 2. T.p.d. of methanol on alkali exchanged X zeolites.

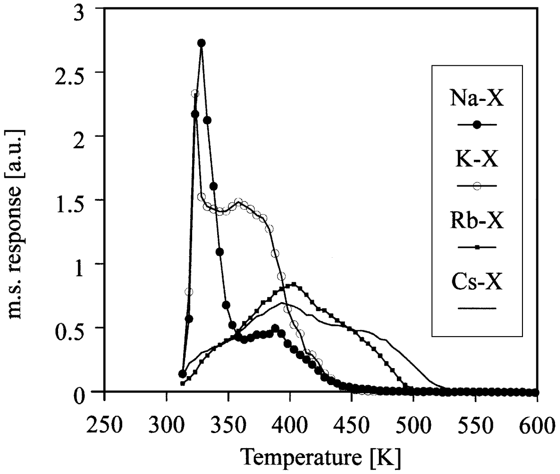


FIG. 3. T.p.d. of toluene on alkali exchanged X zeolites.

(2921–2916 and 2859–2857 cm^{-1}) shift to lower values as the size of the cation increased. In contrast to methanol, the temperature of the t.p.d. maxima of toluene (Fig. 3) increased from Na-X to Cs-X.

3.2. *Coadsorption of the Reactants*

The i.r. spectra recorded after coadsorption of both reactants are compiled in Fig. 4. Only bands characteristic for sorbed methanol and toluene were observed. The bands for sorbed methanol (OH stretching vibration at 3250–3350 cm^{-1} and CH stretching vibrations at 2840–2820 and 2956–2940 cm^{-1}) were the most important ones with Na-X. Indeed, results from the gravimetric experiments showed that in this case, the ratio toluene : methanol on the surface of the catalyst was 1 : 4. On the other hand, the bands characteristic for sorbed toluene (CH stretching vibrations of the aromatic ring at 3055–3045, CH stretching vibrations of the methyl group at 2921–2916 and 2860–2855 and C−C ring vibrations at 1495 and 1598 cm^{-1}) were the main spectral features with Cs and Rb-X. The results from the gravimetric experiments, indicated that with Cs-X the ratio toluene : methanol on the surface of the catalyst was 2 : 1 and with Rb-X it was 4 : 3. The spectrum of toluene and methanol coadsorbed on K-X, was similar to that of Na-X, but the surface concentration of toluene adsorbed was higher. In all cases, the same coadsorbed state was reached irrespectively of the sequence of adsorption of the two reactants indicating reversible adsorption.

TABLE 3

I.r. Bands of Toluene Sorbed on Alkali Exchanged X Zeolites and Intermediate Electronegativity (S_{int}) of the Samples (25)

Sample	$\nu_{\text{C–H aromatic}}$ [cm^{-1}]	$\nu_{\text{C–H aliphatic}}$ [cm^{-1}]	S_{int}
Na-X	3055, 3024	2921, 2859	2.486
K-X	3048, 3023	2917, 2857	2.437
Rb-X	3049, 3022	2916, 2858	2.267
Cs-X	3048, 3021	2916, 2857	2.224

The results from the t.p.d. of toluene and methanol coadsorbed on the various zeolites (compiled in Fig. 5) showed that methanol is the main desorbing species at every temperature with Na-X, while it was toluene with Cs and Rb-X. With K-X, methanol was the main desorbing species until 373 K, but it was toluene at higher temperatures.

3.3. *Reaction Studies*

Below 523 K, reaction products were not detected in the gas phase. At this temperature the formation of formalde-

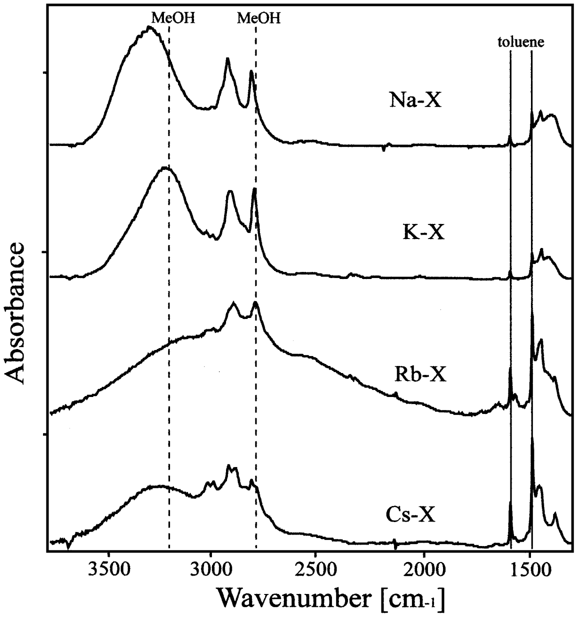


FIG. 4. Difference i.r. spectra after coadsorption of toluene and methanol on alkali exchanged X zeolites ($p = 5 \cdot 10^{-3}$ mbar, $T = 308$ K).

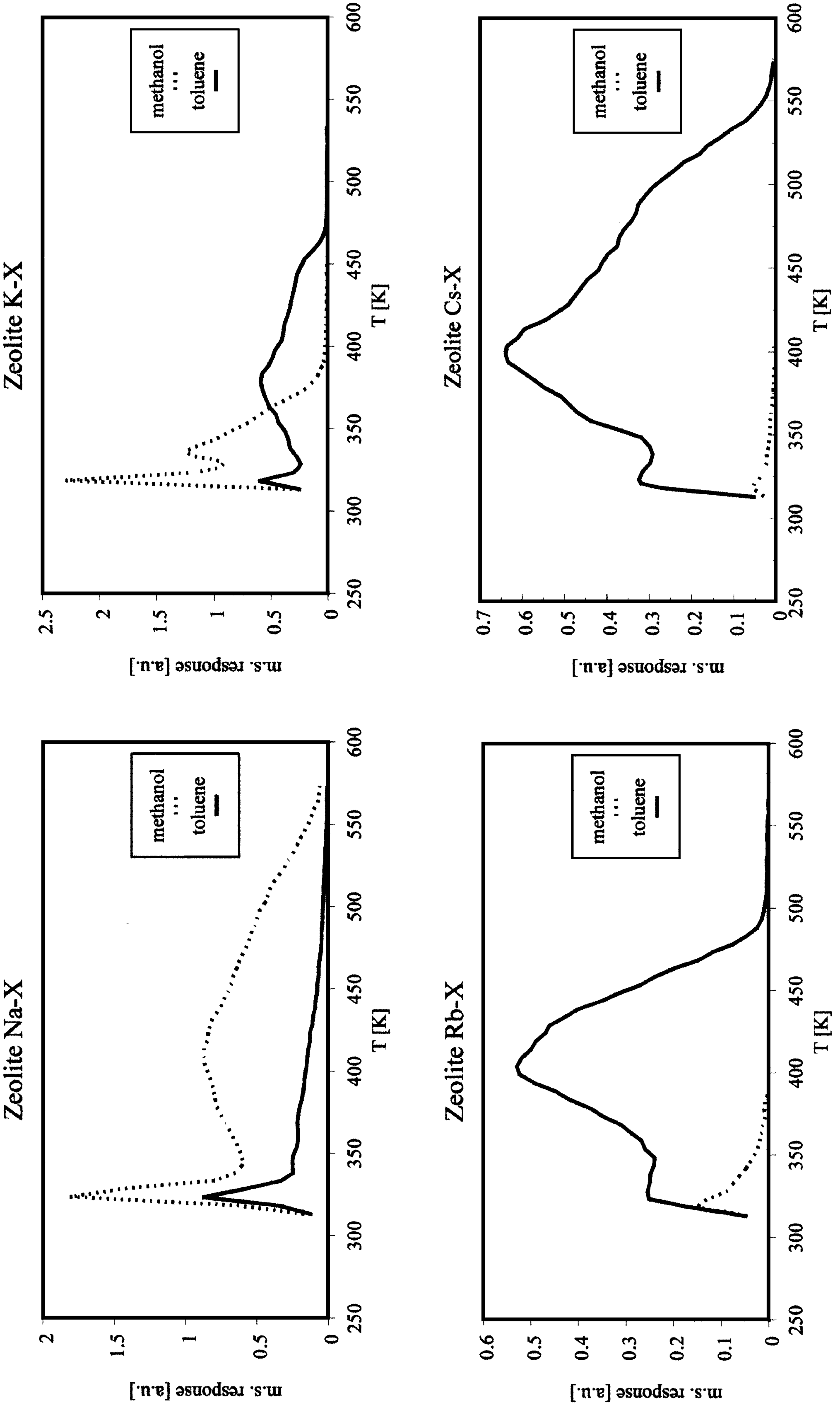


FIG. 5. T.p.d. of toluene and methanol coadsorbed on alkali exchanged X zeolites.

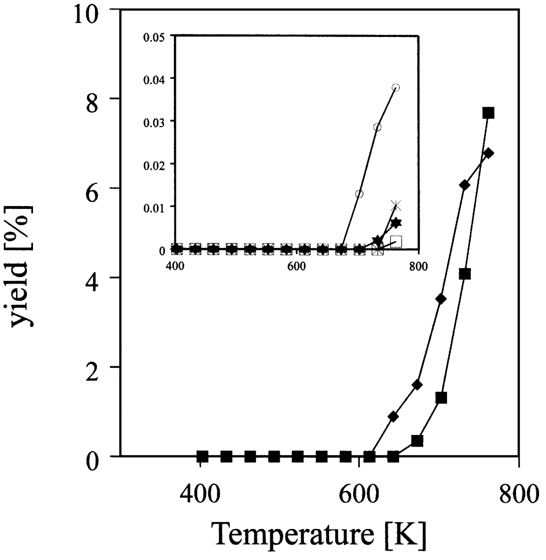


FIG. 6. Effect of reaction temperature in the alklylation with methanol over K-X. Toluene/methanol = 45/15 mbar, 3 mg catalyst, 3.5 ml/min of He as carrier gas: (■) yield of dimethyl ether; (◆) yield of formaldehyde; (□) yield of *p*-xylene; (∗) yield of o-xylene; (★) yield of ethyl benzene; (○) yield of styrene.

hyde and dimethyl ether started to appear with all catalysts studied, getting considerable amounts of these products around 600 K. Alkylation of toluene was observed above 593–653 K. Depending on the composition of the zeolite, side chain or ring alkylated products were formed. A typical evolution of the products is seen in Fig. 6 for K-X. In Fig. 7 the selectivities of the various zeolites (as determined in the reaction at 673 K) are compiled. The zeolites with the larger cations (which preferentially adsorb toluene over methanol) showed high selectivities to styrene and ethylbenzene. The more acidic zeolites (i.e., those with the smaller metal cations, which preferentially adsorb methanol over toluene) showed high selectivity to xylenes. With K-X, xylenes and styrene were formed in similar concentrations.

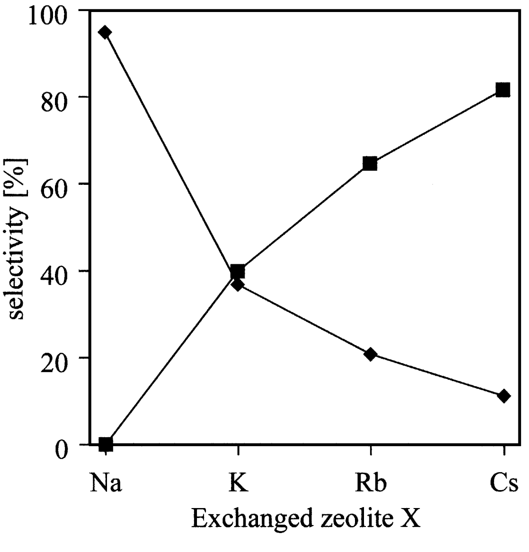


FIG. 7. Selectivity of the alkali-exchanged X zeolites in the reaction of toluene and methanol at 673 K (◆) selectivity towards xylenes, (■) selectivity towards styrene and ethyl benzene.

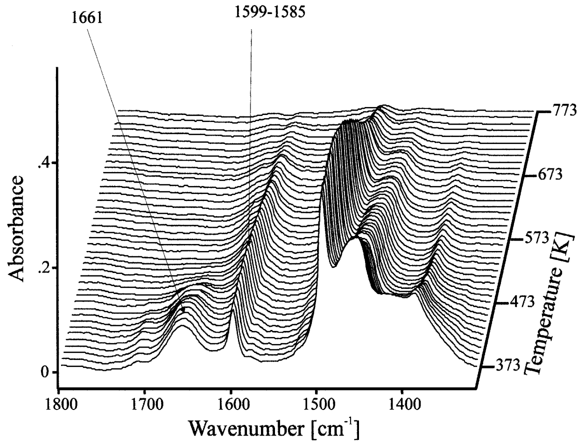


FIG. 8. Difference i.r. spectra of Cs-X during the reaction of toluene and methanol as function of the reaction temperature ($T = 423$–743 K).

The surface species formed during the reaction were monitored *in situ* with i.r. spectroscopy. The spectra obtained for the temperature programmed reaction of toluene and methanol over Cs-X and Na-X are shown in Figs. 8 and 9, respectively. With Cs-X the main sorbant at every temperature was toluene and only one band in addition to those formed for the adsorption of the single compounds was observed at 1661 cm^{-1}. This band reached its maximum intensity at 433 K and disappeared completely at 523 K. At this temperature the formation of formaldehyde and dimethyl ether started. At higher temperatures (when alkylation of toluene was also observed) additional bands were not observed.

The situation was different with Na-X (see Fig. 9), where the main bands observed were typical for sorbed methanol (a broad band around 1400 cm^{-1}), although the concentration of toluene in the gas phase was three times that of

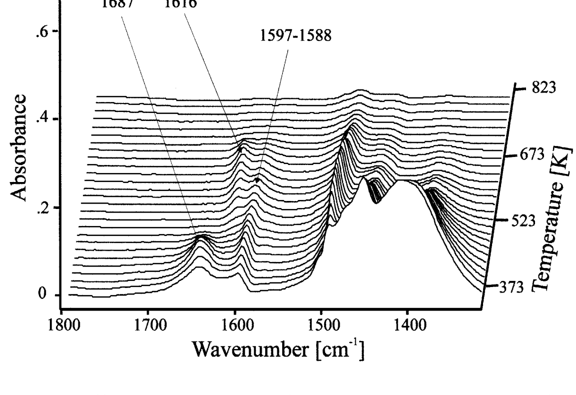


FIG. 9. Difference i.r. spectra of Na-X during the reaction of toluene and methanol as function of the reaction temperature ($T = 423$–743 K).

methanol. At low temperatures (423 K) a new band appeared at 1687 cm^{-1}. This band reached its maximum intensity at 443 K and disappeared completely around 513 K. Again, formaldehyde and dimethyl ether were first detected at that temperature. A second new band at 1616 cm^{-1} appeared, persisting until temperatures as high as 723 K.

4. DISCUSSION

4.1. Sorption and Coadsorption of the Reactants

Upon sorption of methanol the wavenumbers of the OH and CH stretching vibrations decreased, from Na-X to Cs and Rb-X. This trend indicates increasing strength of interaction between the lattice oxygens of the zeolite and the hydrogen atoms of the hydroxyl and the methyl group of methanol and the occurrence of intermolecular interactions of sorbed methanol molecules. Note that this occurs as the electronegativity of the metal cation decreases and, therefore, the base strength increases. However, the results of the t.p.d. of methanol (the desorption maximum of methanol shifted to lower temperatures from Na to Cs-X) show that methanol is bound the stronger the smaller the radius and hence the higher *e/r* ratio of the alkali cation is. The amount of methanol retained upon evacuation prior to TPD indicates that trend also very well. We conclude, thus, that methanol is coordinately bonded *via* the lone electron pair of its oxygen to the cation of the zeolite and the strength of interaction between methanol and the zeolite is mainly determined by this bonding. This bonding should be the stronger the more acidic the cation is, consequently it should be strongest in Na-X. Indeed, this is what has been observed for methanol on alkali exchanged ZSM5, which exhibits very little interactions between the oxygens of the lattice and the hydroxyl proton (23). Strong interactions of the hydroxyl group and the methyl group of the alcohol with the basic lattice oxygens of the zeolite exist for these basic zeolites and the perturbation of the bands increase with increasing base strength of the zeolite. This, permit that at elevated temperatures H_2 is cleaved, results in the formation of formate species at the surface (14, 24).

The i.r. spectra of toluene adsorbed on the various zeolites also showed significant shifts of the C−H stretching vibrational bands of the aromatic ring and the methyl group. As above, these shifts to lower wavenumbers are attributed to stronger interactions with the lattice oxygen, which has an increasingly negative charge when going from Na to Cs-X. The influence of the cation on the charge of the lattice is seen also in other parameters such as, e.g., the decrease of the average electronegativity according to Sanderson (25) (Table 3). The uniformity of the shift suggests that most hydrogen atoms of toluene interact with the lattice oxygens of the alkali exchanged zeolites leading to a multipoint interaction (26) which leads to a polarization of the methyl group.

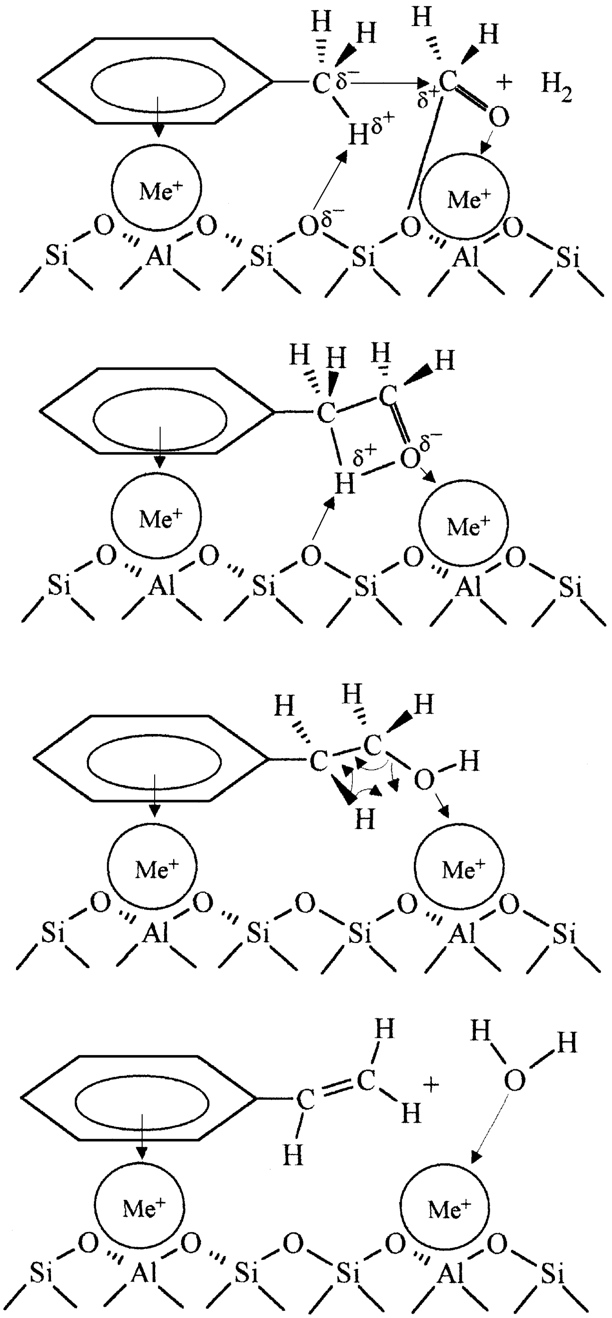
In contrast to methanol, the sorption strength of toluene increases with increasing size of the metal cation, as we conclude from the increasing thermal stability of toluene when going from Na-X to Cs-X. The aromatic molecule is bound *via* its aromatic ring to the metal cation. The better sterical match of the delocalized π-orbitals of toluene and the orbitals of the electron pair accepting alkali cation explains the higher stability of the band with the larger cations. Note that in such a case the higher *e/r* of the smaller alkali cation does not lead to stronger electron pair donor–acceptor interactions, as it was frequently measured in nitrogen base adsorption (27). In consequence, this multipoint adsorption leads to a low mobility of the sorbed aromatic molecules on the alkali-exchanged X zeolites with the larger cations as suggested also by earlier NMR studies (15, 28).

These results were confirmed by the coadsorption studies by which the relative surface concentrations of methanol and toluene reflect the differences in the strength of adsorption of the single compounds as outlined above. As the gravimetric and spectroscopic results showed, methanol is the most abundant sorbed species with Na-X, while toluene is preferentially adsorbed over methanol with Cs-X and Rb-X. The relative surface concentrations of the two reactants on K-X were between these two cases. As only bands characteristic for sorbed methanol and toluene were observed with all zeolites, it is concluded that methanol and toluene coexist independently in the zeolite pores and neither bimolecular complexes nor reaction products are formed under the experimental conditions used.

The different coverages of both reactants on the various zeolites are also reflected in the t.p.d. traces of coadsorbed methanol and toluene. Methanol is the main desorbing species with Na-X and toluene with Cs and Rb-X. These results, indicating that toluene is always preferentially sorbed on the X zeolite exchanged with the largest cations, suggest that the π-electrons of the aromatic nuclei are more perturbed by the high electrostatic field generated by these cations (Rb^+, Cs^+), directing in this way the selectivity toward alkylation of the side chain.

4.2. Chemistry in the Pores of the Zeolite

The results obtained from the *in situ* infrared study of the reaction of toluene with methanol over the various zeolites at different temperatures, confirm again (as the t.p.d. experiments of the coadsorbed samples already suggested) that with Na-X, methanol is the main adsorbant, while with Cs and Rb-X, it is toluene. With all the samples studied, a new band was observed around 1660–1690 cm^{-1} at 433 K. In all cases, the disappearance of this band is correlated with the onset of the formation of formaldehyde in the gas phase. This suggests that the surface species giving raise to this band, might be a precursor for the formation of formaldehyde.



SCHEME 1

At 523 K, when the alkylation of toluene started, the spectra of the different zeolites showed significant differences. With Cs and Rb-X, apart for the relatively intense bands characteristic for sorbed toluene, no additional bands appeared. This indicates that at reaction temperature still a high coverage of toluene remains in the pores of the catalyst. With Na-X, a new band appeared at 1616 cm^{-1} as the band at 1687 cm^{-1} disappeared. Because formaldehyde and dimethyl ether are the only species desorbing, this band might be related to the formation of some type of formate on the catalyst (24). The band is not clearly observed with Cs and Rb-X (although formaldehyde is also formed) due to the predominance of toluene at the surface. All these facts, lead us to the conclusion that the adsorption and activation of toluene (together with the formation of formaldehyde) are the critical factors to initiate the side chain alkylation of the toluene.

The mechanism of the reaction is suggested to be similar to an aldol type condensation (see Scheme 1). Two requirements have to be met, i.e.: (i) methanol has to react with the catalyst to form formaldehyde and formates with a strongly positively polarized C-atom; (ii) the methyl group of toluene has to strongly interact with the basic framework oxygen atoms, activating the aliphatic carbon atom. Under these conditions, the positively polarized C-atom of methanol, may react with the activated carbon atom of toluene leading to the side chain alkylated products. The first point is comparatively easy to obtain and may also proceed on less basic zeolites such as Na^+ exchanged faujasites, but the second condition is only fulfilled with very basic zeolites such as the Cs and Rb exchanged faujasites. Ethylbenzene that is observed seems to be a secondary product resulting from hydrogenation of the primary formed styrene.

5. CONCLUSIONS

In situ i.r. spectroscopic studies of sorbed and coadsorbed toluene and methanol have shown that less basic alkali exchanged zeolites (e.g., Na-X) preferentially sorb methanol over toluene. Methanol interacts primarily *via* the lone electron pair of the alcohol oxygen with the cation of the zeolite and, second, *via* the hydrogens of the OH and the methyl group with the lattice oxygens of the zeolite. In this case, xylenes appear to be the main products formed. More basic zeolites (i.e., Cs and Rb-X) preferentially sorb toluene over methanol. Toluene interacts primarily *via* the electrons of the aromatic ring with the cation of the zeolite and, second, *via* the hydrogens of the methyl group with the lattice oxygens. Here, the main reaction products are styrene and ethyl benzene.

These results suggest that for side chain alkylation three parameters are crucial, i.e., the oxidation of methanol to formaldehyde, the polarization of the methyl group of toluene and the sorption stoichiometry between toluene and the chemisorbed methanol (toluene has to be preferentially adsorbed over methanol). All these requirements are only met with Rb and Cs-X (and partially with K-X), where the side chain alkylation of toluene is proposed to occur *via* a mechanism similar to an aldol-type condensation.

ACKNOWLEDGMENTS

The financial support of the European Community, Human Capital, and Mobility Project, under Grant CIPA-CT94-0184 is acknowledged.

REFERENCES

1. Hattori, H., *Chem. Rev.* **95**, 537 (1995).
2. Dartt, C. B., and Davis, M. E., *Catal. Today* **19**, 151 (1994).
3. Brownstein, A. M., "Chem. Indus. Ser. 5, Catalysis of Organic Reactions," Moser, New York, 1981.
4. Pines, H., and Arrigo, J. T., *J. Amer. Chem. Soc.* **79**, 4958 (1957).
5. Chen, N. Y., Kaeding, W. W., and Dwyer, T., *J. Amer. Chem. Soc.* **101**, 6783 (1979).
6. Kaeding, W. W., Chu, C., Young, L. B., and Butter, S. A., *J. Catal.* **67**, 159 (1981).
7. Young, L. B., Butter, S. A., and Kaeding, W. W., *J. Catal.* **76**, 418 (1982).
8. Yashima, T., Sato, K., Hayasaka, T., and Hara, N., *J. Catal.* **26**, 303 (1972).
9. Sidorenko, Y. N., Galich, P. N., Gutyrya, V. S., Ilin, V. G., and Neimark, I. E., *Dokl. Akad. Nauk. SSSR* **173**, 132 (1967).
10. Engelhardt, J., Szanyi, J., and Valyon, J., *J. Catal.* **107**, 296 (1987).
11. Tanabe, O., Takahashi, O., and Hattori, H., *React. Kinet. Catal. Lett.* **7**(3), 347 (1977).
12. Hathaway, P. E., and Davis, M. E., *J. Catal.* **119**, 497 (1989).
13. Giordano, N., Pino, L., Cavallaro, S., Vitarelli, P., and Rao, B. S., *Zeolites* **7**, 131 (1987).
14. King, S. T., and Garces, J. M., *J. Catal.* **104**, 59 (1987).
15. Sefcik, M. D., *J. Amer. Chem. Soc.* **101**, 2164 (1979).
16. Itoh, H., Hattori, T., Suzuki, K., Miyamoto, A., and Murakami, Y., *J. Catal.* **72**, 170 (1981).
17. Itoh, H., Miyamoto, A., and Murakami, Y., *J. Catal.* **64**, 284 (1980).
18. Itoh, H., Hattori, T., Suzuki, K., and Miyamoto, A., *J. Catal.* **79**, 21 (1983).
19. Eder-Mirth, G., Wanzenbock, H. D., and Lercher, J. A., *Stud. Surf. Sci. Catal.* **94**, 449 (1995).
20. Mielczarski, E., and Davis, M. E., *Ind. Eng. Chem. Res.* **29**, 1579 (1990).
21. Mirth, G., and Lercher, J. A., *J. Phys. Chem.* **95**, 3736 (1991).
22. Mirth, G., Eder, F., and Lercher, J. A., *Appl. Spectrosc.* **48**, 194 (1994).
23. Mirth, G., Lercher, J. A., Anderson, W. A., and Klinowski, J., *J. Chem. Soc. Faraday Trans.* **86**(17), 3039 (1990).
24. Unland, M. L., *J. Phys. Chem.* **82**, 580 (1978).
25. Sanderson, R. T., *J. Am. Chem. Soc.* **105**, 2259 (1983).
26. Freeman, J. A., and Unland, M. L., *J. Catal.* **54**, 183 (1978).
27. Ward, J. W., *J. Catal.* **10**, 34 (1986).
28. Borovkov, V. Y., Hall, W. K., and Kazanski, V. B., *J. Catal.* **51**, 437 (1978).