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In Situ Infrared Study of Alkylation of Toluene with Methanol on Alkali Cation-Exchanged Zeolites

S. T. KING[1] AND J. M. GARCES

The Dow Chemical Company, M. E. Pruitt Building, Midland, Michigan 48674

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The CsX, RbX, and KX zeolites, which selectively alkylate the side chain of toluene with methanol, show formation of both unidentate and bidentate formates on the suface during the reaction. The LiX and NaX, which selectively alkylate the benzene ring, show no formate formation. Bidentate formate can be generated from either the CO reaction with surface OH^- ion or hydrogen reduction of surface CO_3^{2-} carbonate. But the formation of bidentate formate does not correlate with side-chain alkylation. Unidentate formate, which can be formed from the reaction of methanol or formaldehyde, may be an intermediate for side-chain alkylation. The use of carbon dioxide in the feed can stimulate momentarily the alkylation reaction but it also increases coke formation and deactivation.

INTRODUCTION

The direct side-chain alkylation of toluene with methanol may have certain commercial advantages as a styrene process (*1*). The mechanism of this reaction has been investigated by many researchers since the first publication by Sidorenko (*2*). Itoh (*3, 4*) indicated that the acid/base dual site is important for side-chain alkylation in zeolites. But others (*2, 5, 6*) have concluded that the alkylation of the benzene ring and side chain proceeds on acidic and basic sites, respectively.

The zeolite LiX catalyzed only ring alkylation (*4, 5*). The zeolites CsX, RbX, and KX selectively catalyzed side-chain alkylation (*4, 5*). The NaX has been shown by some workers to catalyze side chain alkylation (*5, 7*) and by others to catalyze the benzene ring alkylation (*4, 6*). Since the basicity of Na is between these two groups of alkali cations, the swing of the selectivity of alkylation by NaX may be attributed to differences in acidity during catalyst preparation.

Formaldehyde, which can be produced by the oxidation of methanol, has been proposed to be the side-chain alkylation agent (*2, 3*). The restricted mobility of aromatic adsorbates on CsX has been suggested to play a role in the mechanism of side-chain alkylation (*6*). On the other hand side-chain alkylation occurs using nonzeolite catalysts (*7–9*). The restricted mobility in the zeolite cages cannot be the unique reason for side-chain alkylation.

Surface formate was observed by Unland (*10*) in his IR work when methanol was adsorbed on alkali cation-exchanged zeolites. However, Unland felt that the surface formate, as he observed, could be a dead-end product because it was too stable to be a reaction intermediate.

The purpose of our investigation was to identify the actual structures of the surface species and to determine their function in the alkylation process.

EXPERIMENTAL

Reagent-grade toluene and methanol were obtained from Burdick & Jackson Laboratories, Inc. Deuterated methanol, CD_3–OD, (99% isotopic purity) was obtained from MSD Isotopes. Gaseous formaldehyde was generated by heating paraformaldehyde. Carbon monoxide and carbon dioxide (99.5% purity) were ob-

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[1] To whom correspondence should be addressed.

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tained from Matheson in lecture bottles. All chemicals were used as obtained without further purification.

Zeolite X catalysts were prepared by ion exchange of zeolite 13X at selected pH values, using 0.1–0.5 *M* nitrate or hydroxide solution at room temperature. The catalysts were pressed into 1-cm-diameter wafers for IR studies. The weights of the wafers were in the range of 12–20 mg. The wafer was placed in an IR spectroscopic flow cell as described elsewhere (*11, 12*). The cell was heated to the reaction temperature (150–450°C) and the reactants were fed into the cell. The transmission IR spectra of all the contents (catalyst with the surface species and the reactants in vapor phase) in the cell were recorded durng the reaction using a Digilab FTS-10 spectrometer equipped with a MCT detector. The intensities of the IR absorptions of the vapor phase were negligible due to the short path (0.5 mm) of the cell. All spectra in this paper, except Fig. 1, are ratioed spectra; the IR absorptions due to bulk catalyst were canceled and only the net changes of the surface are shown.

The reaction products were analyzed by on-line gas chromatography using a 6-ft Bentone 34 column. The alkylation feed was a toluene/methanol (Tol/MeOH) mixture with 4/1 mole ratio. The feed was delivered into the cell by a syringe pump at a flow rate of 3 μl/min. The helium flow was 5 cm^3/min and was used to carry the feed through the reaction cell. The used catalysts were regenerated by heating to 420–450°C while purging with air.

RESULTS AND DISCUSSION

The infrared spectra of all the zeolite wafers showed intense bands in the 1640- and 1400-cm^{-1} regions, which indicated the presence of water and carbonates. Water was desorbed easily by heating the samples in a helium stream above 120°C. Decomposition of carbonates started at 150°C. After heating the catalysts for 10 min at 400°C, very little carbonate was left on LiX and NaX (Fig. 1a,b,), but significant amounts of carbonates were still left on CsX, RbX, and KX (Fig. 1c–e) even at 450°C. This indicates that there are significant basicity differences between these two groups of zeolites.

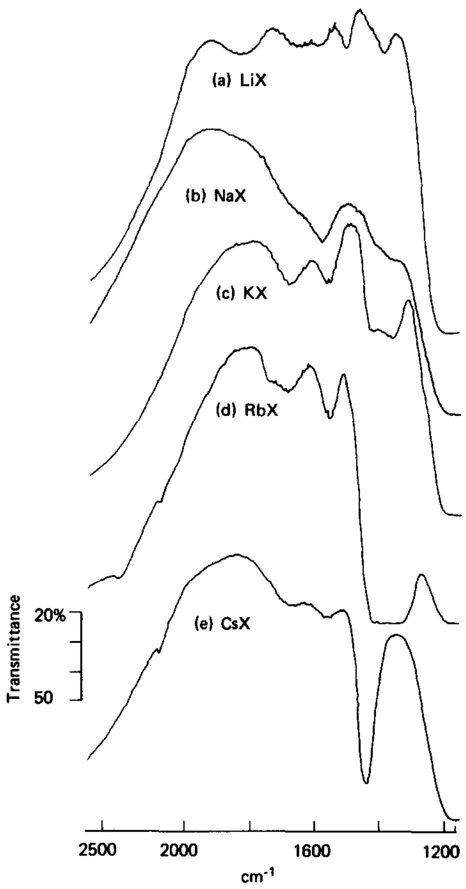


FIG. 1. Transmission IR spectra of zeolite wafers heated to 400°C in a helium stream.

The advantage of using the short-path IR cell in this work is to reduce the interference due to the gas phase IR absorptions during the reaction. Figure 2a shows the IR spectrum of toluene vapor in the reaction cell without catalyst. The weak intensity of the whole spectrum is due to the short path length of the cell. When the zeolite wafer was placed in the cell, the toluene spectrum became much stronger due to the adsorption of toluene on zeolite (Fig. 2b). The reaction of the Tol/MeOH mixture on CsX,

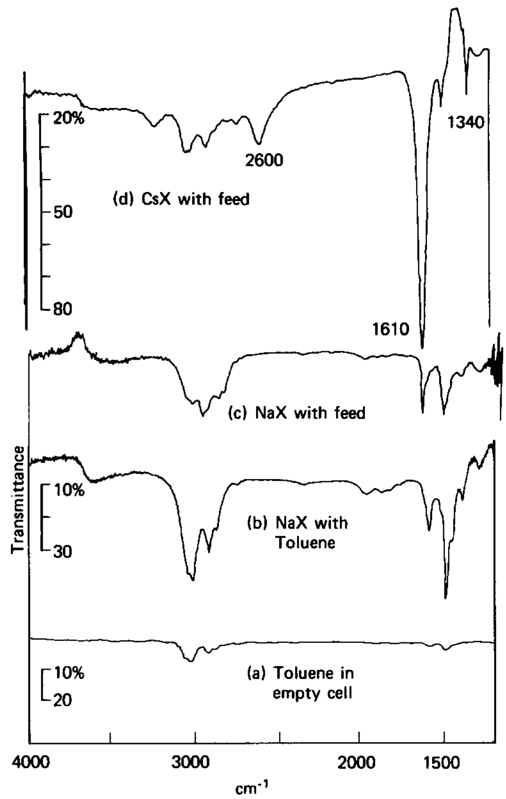
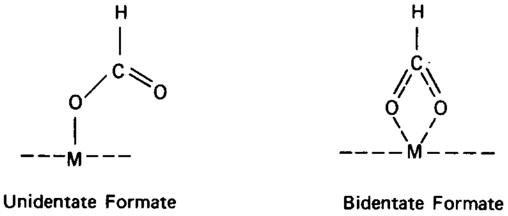


FIG. 2. Infrared spectra as recorded at 420°C. (a) Toluene vapor in empty cell; (b) toluene adsorbed on NaX; (c), (d) reaction of a Tol/MeOH/He feed on NaX and CsX, respectively.

RbX, and KX at 420°C showed different IR spectra than LiX and NaX. Strong IR bands at 1340, 1610, and 2600 cm^{-1} were observed on CsX, RbX, and KX (Fig. 2d) but were not observed on LiX or NaX (Fig. 2c). The toluene conversion was low (1–3%) due to the short contact time and the large amount of unreacted toluene which passed through the void spaces on each side of the catalyst wafer. The concentrations of the alkylated products, as analyzed by GC after 1 h of reaction, are listed in Table 1. In this work, the zeolites NaX and LiX selectively catalyzed ring alkylation to produce xylenes, and the zeolites CsX, RbX, and KX selectively catalyzed side-chain alkylation to produce styrene and ethylbenzene. The *ortho*/*meta*/*para* isomer ratio of the produced xylenes as shown in Table 1 is consistent with published work (*5*).

The IR bands at 1340, 1610, and 2600 cm^{-1} in Fig. 2d are due to the formation of a surface formate from methanol decomposition. The same IR spectra were obtained when methanol was introduced to the clean catalysts at 400°C (Fig. 3a–c). These IR bands are in good agreement with Unland's IR work (*10*). However, as will be discussed later, we have assigned these IR bands to a bidentate formate structure, not the unidentate formate as suggested by Unland (*10*); see Scheme 1. Figure 3d,e shows that very little bidentate formation was formed on NaX or LiX under the same re-



SCHEME 1

TABLE 1

Concentration of the Alkylation Products in the Effluent from the Reaction Cell

	Styrene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
NaX	—	—	0.17	0.08	0.08
RbX	0.11	0.30	—	—	—
CsX	0.47	0.79	—	—	—

Note. The concentration was normalized to 10 mg catalyst. The reaction temperature was 420°C.

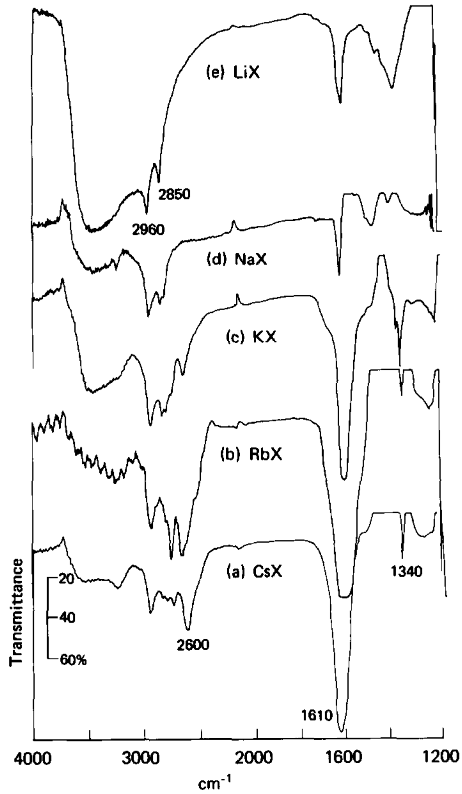


FIG. 3. Infrared spectra of the reacted methanol on zeolites at 400°C.

action conditions. The IR bands at 2850 and 2960 cm^{-1} in Fig. 3 are due to unreacted methanol and the possible formation of surface methoxide groups.

When carbon monoxide was introduced into the cell after the catalysts were regenerated, the same bidentate formate was formed instantaneously on CsX, RbX, and KX at either high (420°C) or low (200°C) temperatures (Fig. 4a–c). Again, very little formate was detected on NaX or LiX (Fig. 4d,e). After carbon monoxide was purged from the cell, decomposition of bidentate formate was monitored by measuring the IR band intensity change at 1610 cm^{-1}. The rate of decomposition was relatively fast at 420°C but no decomposition can be detected below 250°C. Carbon monoxide was the main product produced from this decomposition.

The formation of bidentate formate from CO has to be the result of the interaction of CO with a surface OH group. However, this surface OH cannot be the covalent surface Si–OH group which has a characteristic IR band in the region 3500–3800 cm^{-1}. The interaction of CO with such a covalent surface OH group will show the loss of an IR band (upward band above the base line) in the region 3500–3800 cm^{-1} in the ratioed spectrum. But no such loss can be detected in this region (Fig. 4). It is most likely that CO interacts with OH$^-$ ion to form bidentate formate since the OH$^-$ ion only has a very broad IR absorption in the background and no loss of a sharp band is expected from such an interaction.

Reaction of hydrogen on CsX, RbX, and KX can also generate bidentate formate. But the amount of bidenate formate formed from hydrogen reaction was less than that

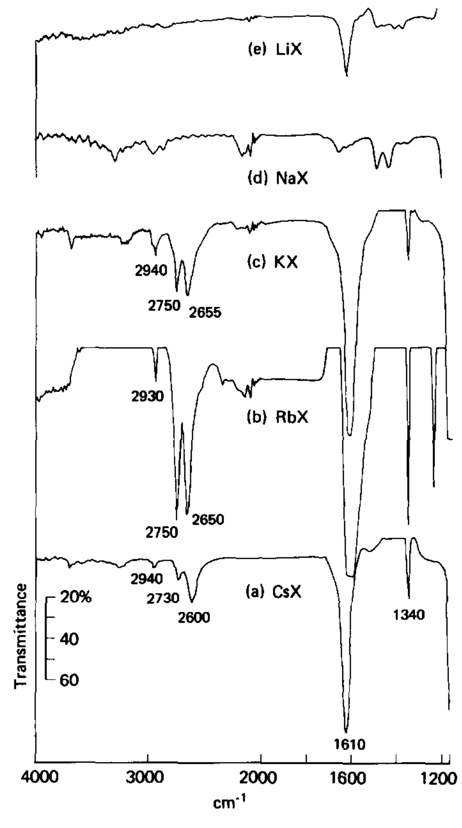


FIG. 4. Infrared spectra adsorbed CO on zeolites at 200°C.

produced from methanol or carbon monoxide. The formation of bidentate formate by reduction with hydrogen was always associated with the intensity loss of the carbonate (CO_3^{2-}) band in the region of 1400 cm^{-1} (Fig. 1). The RbX sample had more residual CO_3^{2-} than the other zeolites (Fig. 1b) and more bidentate formate was observed. Hydrogen reduction of surface CO_3^{2-} is thus another pathway to form bidentate formate.

At a lower temperature (200°C), the reaction of methanol on regenerated CsX, RbX, and KX showed a different surface species. Two intense IR bands at 1685 and 1290 cm^{-1} were observed (Fig. 5a). These two bands belong to the same surface species because the ratio of their intensities is constant at any concentration. As will be discussed later, these two IR bands are assigned a unidentate formate structure. The broad bands at 1450 and 3000 cm^{-1} in Fig. 5a were due to unreacted methanol adsorbed on the zeolites. As long as the cell was filled with excess methanol vapor at this temperature, bidentate formate either did not form or formed very slowly. However, as soon as the methanol was purged from the cell and replaced by helium, bidentate formate formed rapidly (Fig. 5b). Figure 6 shows the IR intensity changes for unidentate and bidentate bands at 1685 and 1610 cm^{-1} under different experimental conditions. Unidentate formate desorbed (or decomposed) slowly at 200°C under helium purge but the stable bidentate formate did not change (Fig. 6c,d). Reintroducing methanol at this point did restore unidentate formate to its original concentration but had no effect on the concentration of bidentate formate (Fig. 6d–f). The bidentate and unidentate formates as shown in Fig. 5 must be formed on different sites. When the cell temperature was increased from 200°C with continuous methanol flow through the cell, the amount of unidentate formate decreased and bidentate formate increased. The amount of bidentate formate reached its maximum at 300°C. Very little unidentate formate was left on the surface at this temperature (Fig. 6f–h). Reducing the temperature from 300 to 200°C in methanol at this point did not lead to reformation of unidentate formate. This additional bidentate formate probably occupied the unidentate formate site.

It is not clear in the above experiment why the excess methanol on fresh zeolite prevents the formation of the bidentate formate at 200°C. One possible explanation is that the methanol decomposed into CO at the unidentate formate site and the excess methanol in the channel blocked the CO interaction with OH^- ion at the bidentate formate site. Another possible explanation is that the methanol was hydrogen bonded on CO_3^{2-} and this isolated CO_3^{2-} cannot react with hydrogen which is generated from the decomposition of unidentate formate.

When carbon monoxide was introduced to replace methanol in the cell at 200°C, unidentate formate was slowly replaced by carbon monoxide to form additional bidentate formate.

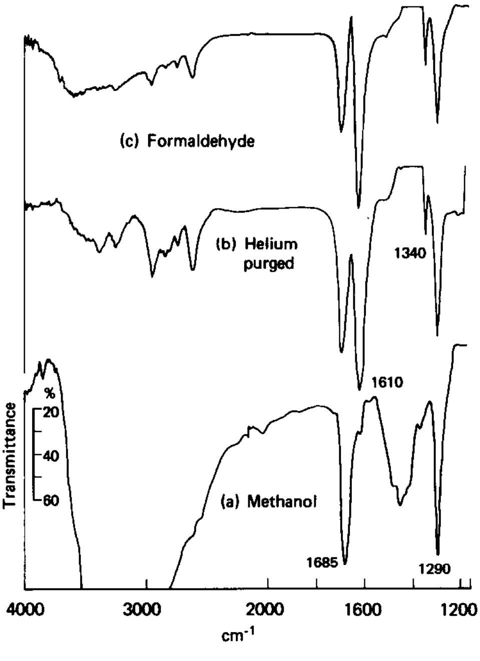


FIG. 5. Infrared spectra of reacted methanol and formaldehyde on CsX at 200°C. (a) Methanol in cell; (b) from (a) after methanol was purged; (c) after formaldehyde reaction on regenerated catalyst.

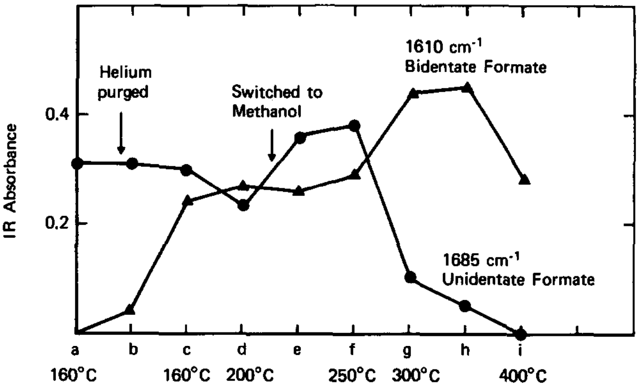


FIG. 6. The changes of unidentate and bidentate formate bands at 1685 and 1610 cm^{-1} on CsX after changes in temperature and feed. (a), (b) Methanol was introduced in cell at 160°C; (b), (c) helium purged at 160°C; (d) temperature was increased to 200°C in a helium stream; (e) methanol was reintroduced at 200°C; (f) temperature was increased to 250°C in methanol; (g) temperature was increased to 300°C in methanol; (h) 10 min at 300°C in methanol; (i) 400°C in methanol.

It should be pointed out that carbon monoxide can generate bidentate formate, but cannot form unidentate formate under any conditions. Also unidentate formate forms only on CsX, RbX, and KX (Fig. 5 and Fig. 7a,b) but not on NaX and LiX (Fig. 7c). The reaction of formaldehyde produced the same unidentate and bidentate formates as produced by methanol (Fig. 5c).

Clearly, the formation of formates on CsX, RbX, and KX correlates with side-chain alkylation. However, surface bidentate formate is not the side-chain alkylation agent. When a CO/H_2/Tol mixture was fed to the catalyst bed at 420°C, no alkylation product was detected and a large amount of bidentate formate was observed. On the other hand there is no evidence to rule out unidentate formate as the active intermediate for side-chain alkylation.

Once bidentate formate is formed on the catalyst surface it does not exchange its hydrogen with deuterium from either D_2 or D_2O even at 420°C. The bidentate *d*-formate can be generated from the reaction of carbon monoxide with the deuterated zeolite surface (Fig. 8). The observed frequency shifts are listed in Table 2. The C–H bands at 2730 and 2600 cm^{-1} shifted to 2010 and 1940 cm^{-1} on deuteration. The 2940-, 1610-, and 1340-cm^{-1} bands all shifted slightly toward lower frequencies.

When CD_3–OD was introduced to the undeuterated catalyst at 160°C, unidentate *d*-formate was observed (Fig. 9b). The C=O stretching band at 1685 cm^{-1} shifted slightly to a lower frequency. But the C–O stretch-

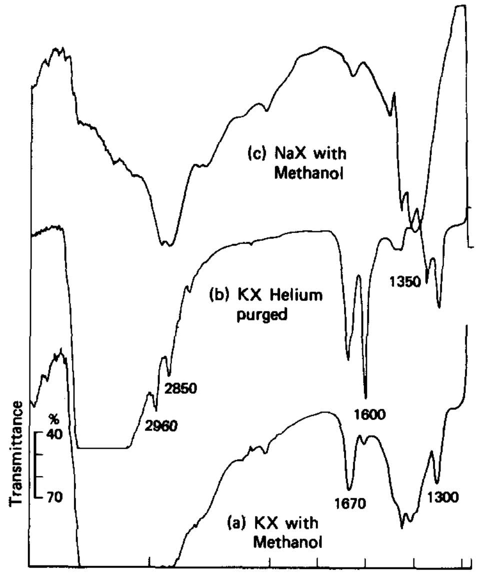


FIG. 7. Infrared spectra of the reacted methanol on zeolites at 200°C. (a) KX with methanol; (b) helium purged from (a); (c) NaX with methanol.

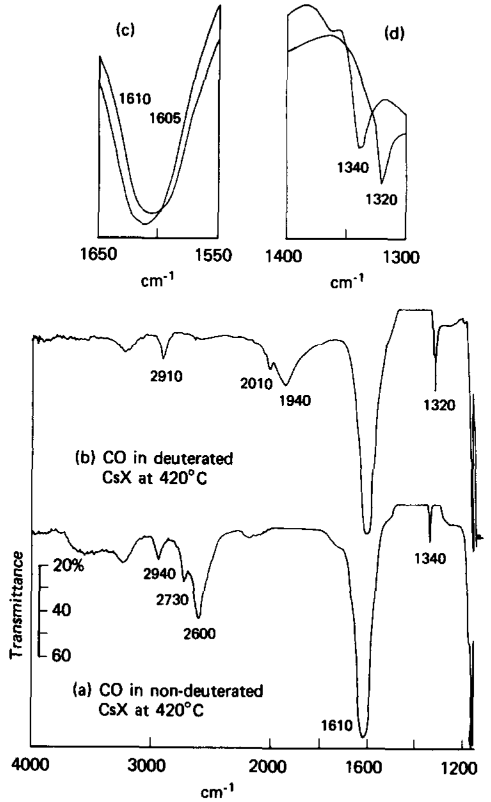


FIG. 8. Infrared spectra as recorded at 420°C. (a) CO on CsX; (b) CO on deuterated CsX; (c), (d) expanded scale in 1610- and 1340-cm^{-1} regions to show the isotopic frequency shifts.

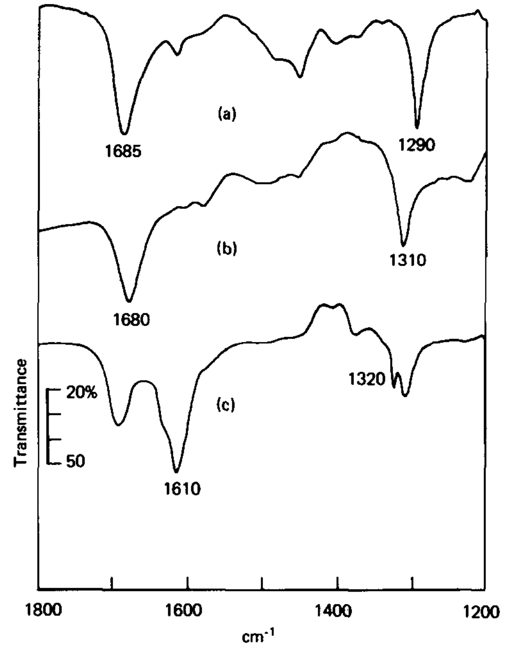


FIG. 9. Infrared spectra was recorded at 160°C. (a) CH_3–OH reaction on CsX; (b) CD_3–OD reaction on CsX; (c) after 30 min, helium purged from (b).

ing band at 1290 cm^{-1} showed a 20-cm^{-1} shift toward a higher frequency (Fig. 9a,b). After the CD_3–OD was purged from the cell, the formation of bidentate *d*-formate was observed as indicated by the appearance of IR bands at 1320 and 1610 cm^{-1} in Fig. 9c. This observation does not necessarily indicate that the C–D bond of bidentate *d*-formate came directly from the CD_3 group of the d_4-methanol because decomposition of d_4-methanol could produce active deuterium to deuterate the surface, and bidentate *d*-formate may be generated from

TABLE 2

Infrared Spectra of Bidentate Formates

	This work					Amenomiya (*14*)			Greenler (*13*)		
	CsX(H)		CsX(D)	RbX	KX	K/alumina			Alumina		
						H		D	H		D
$\nu_2 + \nu_4$	2940	(30)[a]	2910	2930	2940						
ν_1	2730	(720)	2010	2750	2750	2760					
$2\nu_5$	2600	(660)	1940	2650	2650	2680					
a-ν_{OCO} (ν_4)	1610	(5)	1605	1600	1600	1600	(7)[a]	1593	1597	(10)[a]	1587
s-ν_{OCO} (ν_2)	1340	(20)	1320	1350	1350	1350	(24)	1326	1377	(30)	1347

[a] Frequency shift on deuteration.

the D_2 and CO reaction with the deuterated surface.

The early work of Greenler (13) showed the formation of surface bidentate formate from the methanol reaction on alumina. The symmetric (ν_2) and antisymmetric (ν_4) OCO stretching frequencies of this surface species were observed at 1377 and 1597 cm^{-1}, respectively (13). The bidentate formate, as formed on potassium-modified alumina from carbon monoxide adsorption, showed slightly different ν_2 and ν_4 bands at 1350 and 1600 cm^{-1} as observed by Amenomiya and Aleizien (14). The IR spectrum of the bidentate formate on KX as observed in this work is identical to that observed on potassium-modified alumina (Table 2). This suggests that bidentate formates as observed in this work are bonded to alkali cations in zeolites.

In Fig. 8 two C–H bands of bidentate formate at 2600 and 2730 cm^{-1} are observed. Since formate has only one C–H bond, one of these two bands is the C–H stretching fundamental and the other one is the overtone of the C–H bending fundamental at about 1300 cm^{-1}. This C–H bending fundamental was not observed due to its weak intensity. The relatively strong intensity of the overtone mode is due to the Fermi interaction with the C–H stretching fundamental. The 2940-cm^{-1} band in Fig. 8 only showed a slight shift upon deuteration; it should be assigned to the combination mode of the two OCO stretching vibrations.

The shift of the C–O stretching mode of unidentate formate upon deuteration is always toward a higher frequency due to the mixing of the normal modes (15). For example, the C–O stretching frequencies of methyl formate were observed at 1207 and 1213 cm^{-1} for H-$COOCH_3$ and D-$COOCH_3$, respectively (16). The C–O stretching mode of formic acid, H-COOH, at 1105 cm^{-1} shifted at 1143 cm^{-1} in D-COOH (17). In this work, the deuteration causes the C–O stretching mode of unidentate formate to shift from 1290 to 1310 cm^{-1} (Fig. 9 and Table 3). This is strong evidence for the unidentate formate structure. Recent NMR and IR work by Duncan and Vaughan (18) indicated that both unidentate and bidentate formates can be formed on NH_4-Y zeolite.

In one experiment, methanol decomposition was monitored by both IR analysis of the bidentate formate band at 2650 cm^{-1} on the catalyst and GC analysis of carbon monoxide in the gaseous products. Methanol and helium were fed from two separated lines into the IR cell containing the RbX wafer at 400°C. During the steady state of the reaction, a relatively high concentration of CO was observed compared to surface bidentate formate concentration (0 to 10 min in Fig. 10). The CO concentration dropped off sharply as soon as the methanol was switched off from the feed (at 10 min in Fig. 10), but the surface bidentate formate decomposed slowly. After methanol was purged from the cell the decomposition curve of bidentate formate correlates very well with the CO production curve (10 to 30 min in Fig. 10). This indicates that the major methanol decomposition is either not at the bidentate formate site or only at a small percentage of the bidentate formate sites on the outer part of the zeolite crystallite.

TABLE 3

Infrared Spectra of Unidentate Formates

	This work				Susi (16)			Millikan (17)		
	CsX(H)		CsX(D)	KX	H-$COOCH_3$		D-$COOCH_3$	H-COOH		D-COOH
C=O stretching	1685	(5)[a]	1680	1670	1754			1770	(14)[a]	1756
C—O stretching	1290	(−20)	1310	1300	1207	(−6)[a]	1213	1105	(−38)	1143

[a] Frequency shift on deuteration.

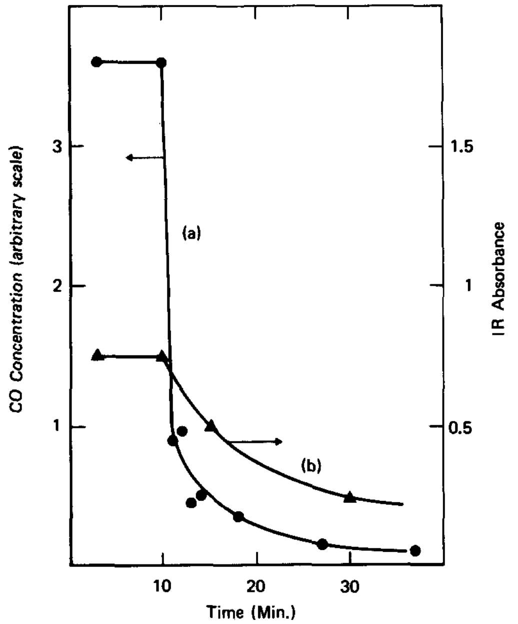


FIG. 10. Methanol decomposition on RbX at 400°C. (a) CO in gaseous products; (b) IR absorbane of the surface bidentate formate band at 2650 cm^{-1}.

At 200°C, bidentate formate did not react with water or air. But carbon dioxide did replace the bidentate formate rapidly to form a surface carbonate (Fig. 11b). This carbonate may have an unidentate or bidentate structure (*14*) and it decomposed quickly when purged with helium. The unreactive bidentate formate may occupy useful alkylation sites. The addition of high concentration of carbon dioxide may help reopen those sites. When helium in the Tol/MeOH/He feed was changed to carbon dioxide, a rapid increase of styrene production was observed (Fig. 12). This seems to indicate the cleaning effect of carbon dioxide. However, this increase in styrene production was followed by rapid catalyst deactivation (Fig. 12).

Without additional CO_2 when Tol/MeOH/He feed was used, slow catalyst deactivation was observed in the first hour of reaction. This deactivation was accompanied by the formation of an aliphatic "coke" as indicated by the formation of a 2920-cm^{-1} band on the catalyst (Fig. 13a, b, e, f). During fast deactivation when carbon dioxide was used in the feed, the formation of an aromatic coke, as indicated at 3050 cm^{-1} (Fig. 13c), was observed. Coke formation also correlated with the decrease in the transparency of the catalyst wafer. This indicated the formation of a carbon deposit. The RbX sample showed a higher level of residual CO_3^{2-} than other zeolites (Fig. 1d). The 3050-cm^{-1} band was observed on RbX after ½-h reaction with the Tol/MeOH/He feed (Fig. 13f). However, when carbon dioxide was used, the 3050-cm^{-1} band intensity increased much more rapidly (IR absorbance changed from 0.36 to 0.6). At the the same time the catalytic activity decreased rapidly (Fig. 12b) and the catalyst became very opaque. CsX did not deacti-

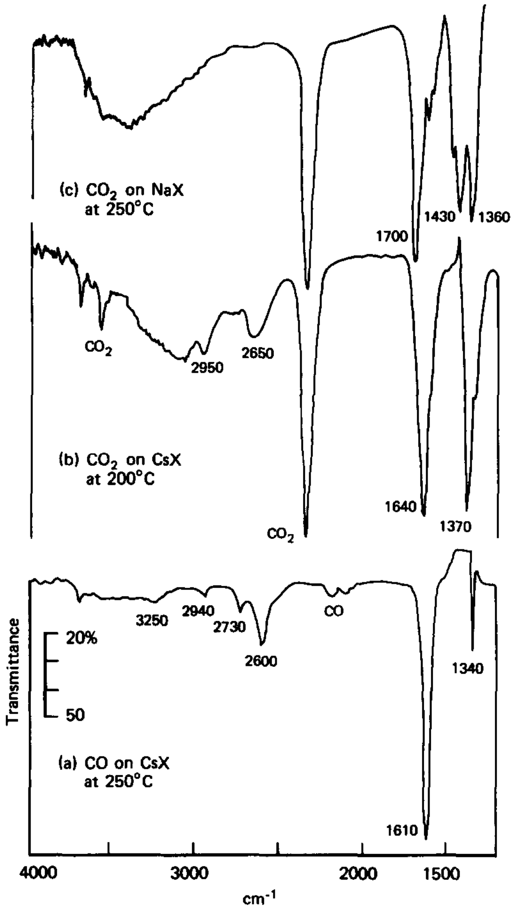


FIG. 11. Infrared spectra of (a) CO on CsX at 250°C; (b) CO_2 on CsX at 200°C; (c) CO_2 on NaX at 250°C.

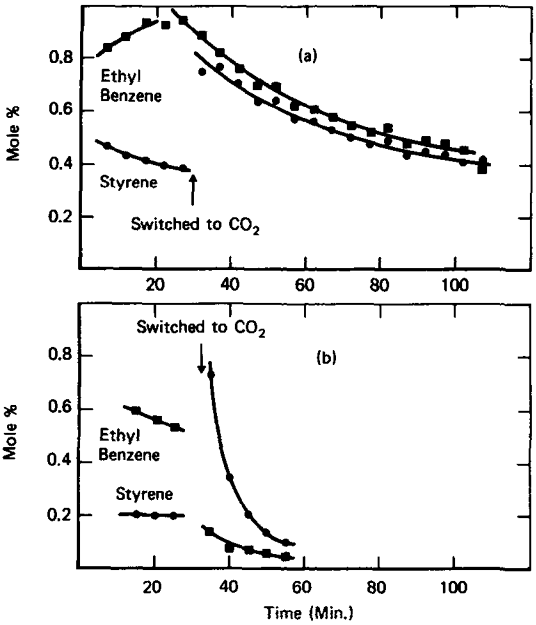


FIG. 12. Changes of styrene and ethylbenzene concentrations in the product stream when helium was switched to CO_2 in the feed. (a) 20.5 mg CsX at 420°C; (b) 18.5 mg RbX at 420°C.

vate as fast as RbX when carbon dioxide was used. The fomation of the 3050-cm^{-1} band on CsX was also slower than on RbX (Fig. 13c).

Carbon dioxide caused an increase in xylene production. But it also caused slow catalyst deactivation (Fig. 14). However, very little "aromatic coke" was observed on NaX (Fig. 13e). Carbon dioxide adsorption on NaX showed somewhat different carbonates than that of CsX (Fig. 11c).

SUMMARY

The molecular structures of unidentate and bidentate formates have been identified on CsX, RbX, and KX zeolites. Under the same reaction conditions, very little formate can be detected on LiX and NaX, which selectively catalyze ring alkylation.

Bidentate formate can be formed either by CO reaction with surface OH^- ion or by hydrogen reduction of surface CO_3^{2-}. It is not very clear whether the bidentate formate can be formed directly from methanol

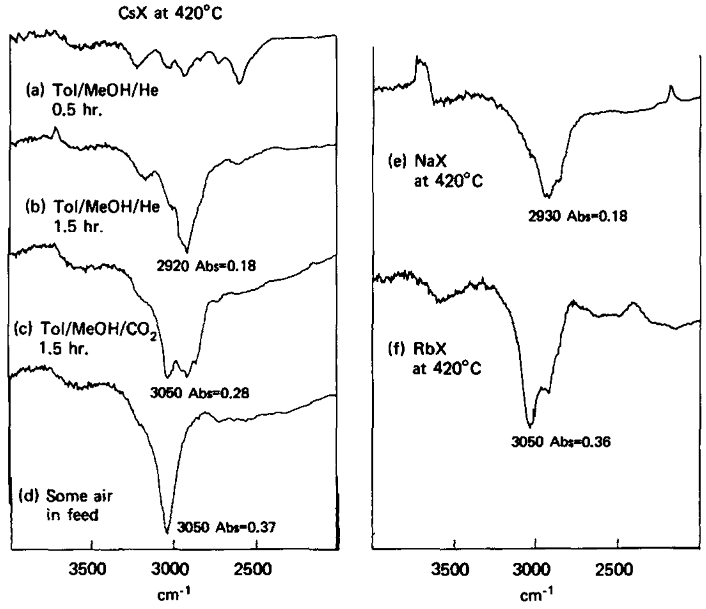


FIG. 13. Infrared spectra of "coke" after reaction at 420°C. (a) 30 min after the reaction of the Tol/MeOH/He feed on CsX; (b) 1 h from (a); (c) after 1.5 h reaction of the Tol/MeOH/CO_2 feed on CsX; (d) on CsX, after a small amount of air was leaked into the Tol/MeOH/He feed; (e) NaX, after 1.5 h reaction with Tol/MeOH/He and Tol/MeOH/CO_2 feeds; (f) RbX, after 0.5 h reaction with the Tol/MeOH/He feed.

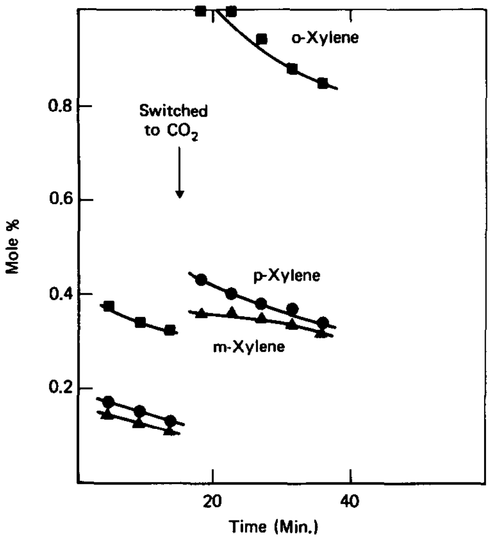
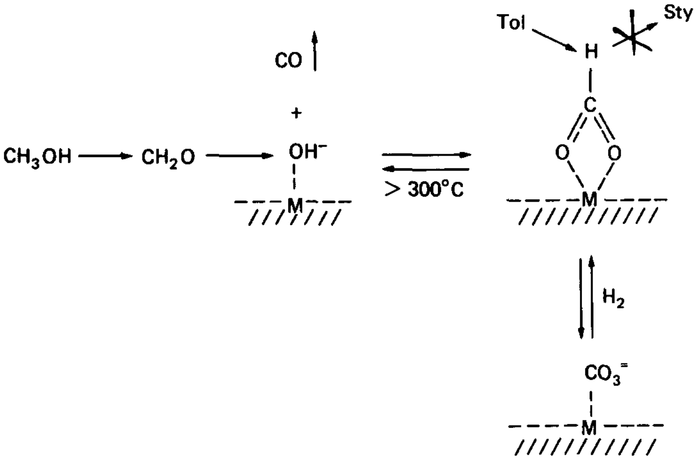


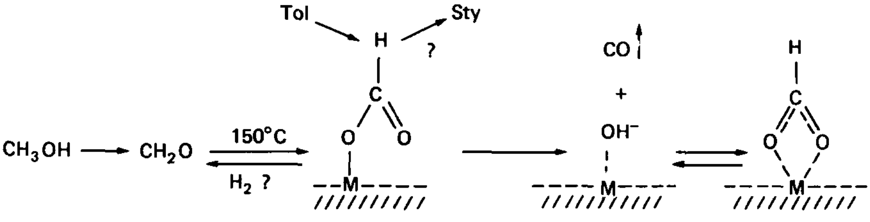
FIG. 14. Change of the xylene production after helium was switched to CO_2 in the Tol/MeOH/He feed; 18.3 mg of NaX at 420°C.

or formaldehyde. Most likely, the methanol or formaldehyde was decomposed into hydrogen and carbon monoxide first and the bidentate formate was formed from the subsequent surface reactions of carbon monoxide and hydrogen. Bidentate formate does not react with toluene and is probably not the intermediate for side-chain alkylation; see Scheme 2.

Unidentate formate can be formed from the reaction of methanol or formaldehyde on KX, RbX, and CsX zeolites but not from CO. It is most likely that this undentate formate site is responsible for the rapid methanol decomposition into CO and it may also play an important role in side-chain alkylation. The selective side-chain alkylation is always associated with high rates of carbon monoxide and formaldehyde production (*4*); see Scheme 3.



SCHEME 2



SCHEME 3

The formation of CO_3^{2-} carbonate and formation of formates are interrelated since they all are bonded to the same alkali cations. The results indicate that carbon dioxide can affect the stability of bidentate formate. Addition of carbon dioxide in the feed seems to stimulate styrene production. However, such stimulation generates aromatic coke which causes catalyst deactivation. Carbon dioxide also stimulates xylene production on NaX. The increase of xylene production may be due to the carbon dioxide poisoning of the basic sites on NaX leading tó a more acidic catalyst.

REFERENCES

1. Kollar, J., *Adv. Chem. Technol.* **1,** 1 (1979).
2. Sidorenko, Y. N., Galich, P. N., Gutyrya, V. S., Ilin, V. G., and Neimark, I. E., *Dokl. Akad. Nauk SSSR* **173,** 132 (1967).
3. Itoh, H., Miyamoto, A., and Murakami, Y., *J. Catal.* **64,** 284 (1980).
4. Itoh, H., Hattori, T., Suzuki, K., and Murakami, Y., *J. Catal.* **79,** 21 (1983).
5. Yashima, T., Sato, K., Hayasaka, T., and Hara, N., *J. Catal.* **26,** 303 (1972).
6. Sefick, M. D., *J. Amer. Chem. Soc.* **101,** 2164 (1979).
7. Garces, J. M., Vrieland, G. E., Bates, S. I., and Scheidt, F. M., *in* "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), p. 67 Elsevier Amsterdam/New York, 1985.
8. Tanabe, K., Takahashi, O., and Hattori, H., *React. Kinet. Catal. Lett.* **7,** 347 (1977).
9. Sodesawa, T., Kimura, I., and Nozaki, F., *Bull. Chem. Soc. Japan* **52,** 2431 (1979).
10. Unland, M. L., *J. Phys. Chem.* **82,** 580 (1978).
11. King, S. T., *Appl. Spectrosc.* **34,** 623 (1980).
12. King, S. T., and Strojny, E. J., *J. Catal.* **76,** 274 (1982).
13. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
14. Amenomiya, Y., and Pleizier, G., *J. Catal.* **76,** 345 (1982).
15. Susi, H., and Scherer, J. R., *Spectrochim. Acta* **25,** 1243 (1969).
16. Susi, H., and Zell, T., *Spectrochim. Acta* **19,** 1933 (1963).
17. Millikan, R. C., and Pitzer, K. S., *J. Chem. Phys.* **27,** 1305 (1957).
18. Duncan, T. M., and Vaughan, R. W., *J. Catal.* **67,** 469 and 49 (1981).