

Base Catalysis by Alkali Modified Zeolites

III. Alkylation with Methanol

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Ion exchanged CsNaX and CsNaY, cesium acetate impregnated CsNaX (CsAce/CsNaX) and CsNaY (CsAce/CsNaY), and MgO have been reacted with isopropanol at 425°C and atmospheric pressure to assess their acid/base properties at a temperature consistent with that used in the side chain alkylation of toluene with methanol. The results suggest that the ability of the catalysts tested here to promote a base mediated reaction follow the order of



Selectivities to acetone measured at 4.73% conversion follow this order as well, ranging from 95.7% and 93.9% for MgO and CsAce/CsNaY, respectively, to 17.6% for the CsNaX. Thus, these catalysts can be grouped into two categories: (i) catalysts which vary in acid/base properties yet possess identical topology (e.g., the zeolites) and (ii) catalysts which vary in topology yet have similar acid/base properties (e.g., MgO and CsAce/CsNaY). These catalysts were compared using the side chain alkylation of toluene, ethane, methane, and acetone with methanol. For the impregnated zeolites, similar toluene conversions were observed. Unlike the impregnated X zeolite, no formaldehyde (i.e., the alkylating agent) was observed in the product stream of the impregnated Y zeolite. Both MgO and CsAce/CsNaY had similar methanol decomposition products; i.e., no formaldehyde and high CO formation, yet unlike CsAce/CsNaY no toluene conversion was observed for MgO. No conversion of ethane or methane was observed for either impregnated zeolite at 425°C. Attempts at higher temperatures (e.g., 465°C) failed also. Acetone was alkylated to methyvinylketone and methylethylketone; however, the majority of the reacted acetone formed products which appear to result from acetone aldol condensations. © 1989 Academic Press, Inc.

INTRODUCTION

Recently, we reported on the development of alkali modified zeolites as base catalysts (1, 2). Impregnation of CsNaY with cesium acetate (CsAce/CsNaY) improved the intrinsic rate of isopropanol decomposition to acetone at 350°C by an order of magnitude above that observed from the untreated CsNaY. However, impregnation of CsNaX with cesium acetate (CsAce/CsNaX) promoted the acetone activity only slightly above that of the untreated CsNaX and was comparable to the rate obtained from the untreated CsNaY. Furthermore, the selectivities to acetone were 97.4 and

61.6% for CsAce/CsNaY and CsAce/CsNaX, respectively. When the rates of acetone formation were normalized per unit surface area, MgO and CsAce/CsNaY gave equivalent values. Studies aimed at elucidating the nature of the active site on CsAce/CsNaY (2) suggested that the cesium acetate decomposed to form cesium oxide, and it was the oxide which was suspected to be the active site for acetone formation. Evidence was presented also to indicate the presence of an isopropoxide intermediate which was responsible for the minor amounts of propylene formed over the CsAce/CsNaY catalyst. Thus, the CsAce/CsNaY catalyst possessed (i) significantly higher activity for the formation of acetone from isopropanol (normally attrib-

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uted to base sites), and (ii) virtually no Brønsted acid sites.

The alkylation of toluene with methanol has been studied extensively over a variety of catalysts (3–9). It is generally accepted that in the side chain alkylation of toluene, methanol is dehydrogenated to formaldehyde and it is the formaldehyde which serves as the alkylating agent to form styrene. Note that an undesirable side reaction is the hydrogenation of styrene to ethylbenzene. CsNaX zeolites impregnated with boric acid (5, 9) and/or copper nitrate (10) appear to be the most effective catalysts for side chain alkylation. Several factors have been suggested to play important roles for side chain alkylation to occur: (i) active base sites, (ii) spatial constraints found within the zeolite pores, and (iii) stabilization of the formaldehyde. Although considerable evidence is available to show that strong acid sites result in ring alkylation to xylenes (4, 7, 11, 12), a certain degree of acidity is thought to promote the stability of the formaldehyde (9, 13).

The objective of this work is to study the alkylation of toluene, acetone, ethane, and methane with methanol using the novel base catalyst we developed previously, CsAce/CsNaY (1, 2), and to make a direct comparison between the alkylation results and those obtained from isopropanol decomposition.

EXPERIMENTAL SECTION

Materials. The synthesis of zeolites X and Y and the ion exchange procedures used have been previously described (1). After exchange, the CsNaX and CsNaY zeolites were rinsed with deionized water to remove the possibility of salt occlusion. The materials were then dried at 100°C in a convection oven. These solids will be denoted as untreated CsNaX and CsNaY. Magnesium oxide was formed by the *in situ* dehydroxylation of Mg(OH)₂ in helium at 550°C. Isopropanol, toluene, acetone, and methanol were purchased from Aldrich and all possessed purities of greater than 99.9%.

Ethane, methane, and helium were obtained from AIRCO at greater than 99.9% purity. Prior to impregnation, the exchanged solids were rinsed with a 0.01 N solution of cesium acetate to remove the possibility of salt occlusion yet minimize decationation.

Impregnation. Cesium acetate impregnation was accomplished by micropipetting 0.025 N cesium acetate into a round bottom flask. Subsequently, the dried, acetate rinsed CsNaX or CsNaY was added so that a precalculated loading (~2.5 cesium acetate molecules per unit cell or 2.8 wt% for CsNaY) could be obtained upon removal of the water. The flask was mounted onto a rotovap and rotated for ~8 h at 25°C and 1 atm. Finally, vacuum was applied and the temperature elevated to 40°C to remove bulk water and leave the cesium acetate occluded in the zeolites (*vide infra*).

Analysis. Thermogravimetric analyses (TGA) were performed on a Dupont 951 thermogravimetric analyzer. Argon adsorption isotherms were obtained using the Omnisorp 100 system developed by Omicron Technology. Superficial analyses of the zeolites for silicon (Si_{2p}) and cesium (Cs_{3d}) were performed by X-ray photoelectric spectroscopy (XPS) with a Perkin-Elmer Phi 5300 ESCA which employed a MgK α X-ray source. Several bulk chemical analyses of the zeolites for Si and Cs were obtained from Galbraith Laboratories, Inc. (Knoxville, TN), while other zeolite samples were analyzed for cesium, sodium, and aluminum in our laboratories on a Jarrell-Ash 9000 inductively coupled argon plasma spectrometer.

Reactor system. Liquid reactants were fed by a syringe pump into a 160°C constant temperature vaporizer where they were mixed with gas phase reactants and/or helium. The heated reactant stream was able to bypass or feed into a vertical, downflow, fixed bed microreactor. For isopropanol decomposition, the microreactor consisted of a 3-mm-i.d. Vycor tube placed inside a tube furnace. Alkylation experiments required

larger loadings of catalyst and a 10-mm-i.d. quartz tube was employed. During the alkylation runs, two thermocouples located at the center of the catalyst bed and at the outside wall of the quartz tube were used to monitor the temperature. A temperature gradient of $\sim 10^\circ\text{C}$ was typically observed and the temperatures reported here are the averages. Isopropanol decomposition products were monitored by online gas chromatography. Alkylation reaction products were analyzed by (i) injection of liquid products collected in a liquid nitrogen trap and (ii) injection by an online gas sampling valve.

Procedure. The catalysts were compacted without binder into pellets. These pellets were crushed and size separated to either $-60/+80$ mesh (isopropanol decomposition) or $-35/+60$ mesh (alkylation). As with our previous work (1, 2), contact times are based upon the number of zeolite unit cells rather than weight. MgO is compared to the zeolite catalysts on the basis of surface area. MgO and the impregnated CsNaY have BET surface areas of 125 and $492\text{ m}^2/\text{g}$, respectively.

The conditions used for isopropanol decomposition studies are: isopropanol and helium flow rates of 45 and 180 cm^3 (STP) per min, respectively, $T = 425^\circ\text{C}$, and the catalyst charge-to-reactant flow (W/F) = 6.13×10^{-6} mole zeolite unit cell \cdot h \cdot (mole isopropanol) $^{-1}$. For the comparison between MgO and CsAce/CsNaY, $W/F = 52\text{ m}^2 \cdot \text{h} \cdot$ (mole isopropanol) $^{-1}$. Note that the contact time used here for MgO is identical to that used previously for CsAce/CsNaY when normalized on a per surface area basis. The yields and selectivities reported here for isopropanol decomposition runs are defined as $Y_i =$ moles of i formed per mole of isopropanol fed times 100%, $S_i =$ moles of i formed per mole of isopropanol reacted times 100%, where i represents either acetone or propylene.

For the alkylation of toluene, acetone, ethane, and methane, the substrate-to-methanol ratio is 5, the helium-to-total re-

actant ratio is 5, and the reaction temperature varied from 380 to 465°C . The substrate and methanol flow rates are 12.8 and 2.6 cm^3 (STP) per minute, respectively, and $W/F = 1.45 \times 10^{-3}$ mole zeolite unit cell \cdot h \cdot (moles of substrate and methanol) $^{-1}$. For the comparison between MgO and CsAce/CsNaY, $W/F = 1.23 \times 10^4\text{ m}^2 \cdot \text{h} \cdot$ (moles of toluene and methanol) $^{-1}$. Again, the contact time used for MgO is identical to that used for CsAce/CsNaY based upon surface area. Conversions, yields, and selectivities are defined as $C_i =$ moles of substrate reacted per mole of substrate fed times 100%, $Y_i =$ moles of i formed per mole of substrate fed times 100%, $S_i =$ moles of i formed per moles of total products formed times 100%. For the methanol decomposition products, e.g. CO, CO_2 , dimethylether (DME), and formaldehyde, yields are defined as $Y_i =$ moles of i formed per mole of methanol fed times 100%. The production of H_2 was not monitored.

RESULTS

The Si/Al ratio, the percent exchange, and the molecular weight per unit cell of the untreated zeolites were determined from bulk chemical analysis and are listed in Table 1. Because of the low levels of impregnation (~ 2.5 cesium acetate molecules per unit cell) the difference in molecular weight between the untreated and the impregnated zeolites is assumed to be 480 g/mole or 2.5 times the formula weight (approximate verification was obtained by monitoring the weight loss from the combustion of the acetate molecules by TGA).

Figure 1 shows the acetone and propylene yields obtained from the untreated and from the impregnated CsNaY and CsNaX zeolites at 425°C and constant W/F . For the X catalysts, an increase in acetone yield from 0.46 to 1.05% is observed with impregnation. Furthermore, the propylene yield fell from 3.29 to 1.46%. The impregnation of CsNaY proved to be far more effective in promoting the yield of acetone and is

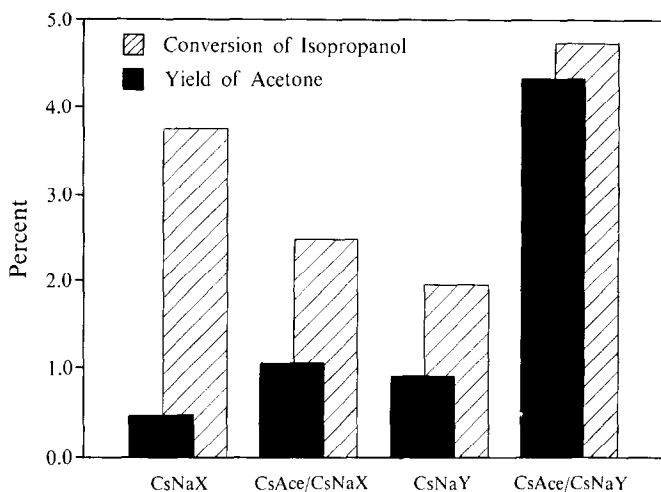


FIG. 1. Conversion of isopropanol and yield of acetone at constant contact time. $W/F = 6.13 \times 10^{-6}$ mole zeolite unit cell \cdot h \cdot (mol isopropanol) $^{-1}$, temperature = 425°C, total pressure = 1 atm, and partial pressure of isopropanol = 152 Torr.

consistent with our earlier work (1, 2). For the untreated and impregnated CsNaY zeolite, the acetone yield rose from 0.92% to 4.33%, respectively. As was observed for the X zeolite, propylene yields decline as a result of impregnation (1.05 to 0.28%).

Figure 2 illustrates the selectivity to acetone at 425°C and constant conversion for the untreated and for the impregnated zeolites at an isopropanol conversion of 4.73%. The selectivity to acetone increases from 17.6% for the untreated CsNaX zeolite to 93.9% for the impregnated CsNaY zeolite.

At a constant W/F (surface area basis), the yield of acetone for MgO is 9.12% while that for CsAce/CsNaY is 4.73%. The yields of propylene are fairly similar at 0.28 and 0.37% for the CsAce/CsNaY and MgO, respectively, while the selectivities to acetone at a conversion of 4.73% are 93.9 and 95.7%, respectively.

Figure 3 shows the conversions of toluene and yields of styrene from the untreated and impregnated zeolites at a constant W/F and at a reaction temperature of 437°C. For both the X and Y zeolites, a

TABLE I
Physical Data of Zeolite Catalysts

Catalyst	Si/Al	% Exchanged ^{a,b}	Molecular wt. per unit cell ^c	Cesium acetate per unit cell
CsNaX	1.34	60	18710	—
CsAce/CsNaX	1.34	60	19190	~2.5
CsNaY	2.34	64	16870	—
CsAce/CsNaY	2.34	64	17350	~2.5

^a Based on a unit cell composition of NaY: $\text{Na}_{58}\text{Al}_{58}\text{Si}_{134}\text{O}_{384}$; NaX: $\text{Na}_{82}\text{Al}_{82}\text{Si}_{110}\text{O}_{384}$.

^b Zeolites exchanged with cesium acetate.

^c Dehydrated.

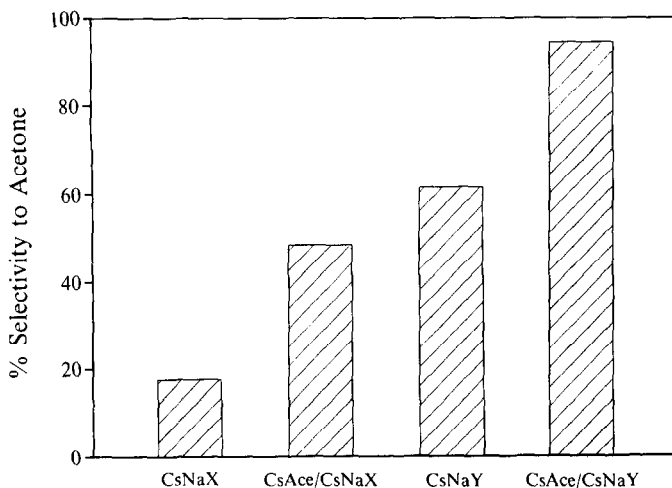


FIG. 2. Selectivity to acetone at constant isopropanol conversion. Conversion = 4.73%, temperature = 425°C, total pressure = 1 atm, and partial pressure of isopropanol = 152 Torr.

significant increase in toluene conversion is observed with impregnation. Furthermore, trace amounts of xylenes are observed only from the untreated CsNaY catalyst.

Figure 4 shows the influence of the reaction temperature on toluene conversion. As observed in Fig. 3, the conversion of toluene is slightly higher for CsAce/CsNaY than CsAce/CsNaX. For both zeolites, the

toluene conversion obtains a maximum at 425–435°C. Figs. 5A and 5B illustrate the yields of methanol decomposition products for the impregnated zeolites as a function of the reaction temperature. For the CsAce/CsNaX zeolite, dimethyl ether (DME) and formaldehyde are observed in the product stream. For the CsAce/CsNaY zeolite, only trace amounts of formaldehyde and

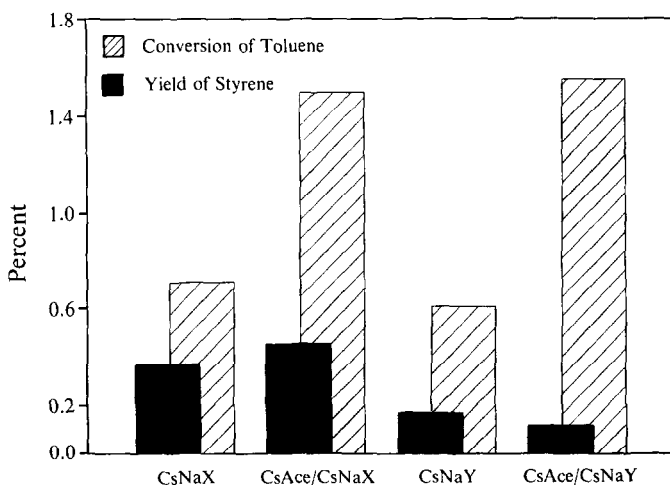


FIG. 3. Effect of catalyst on toluene conversion and styrene yield. $W/F = 1.45 \times 10^{-3}$ mole zeolite unit cell \cdot h \cdot (moles of toluene + methanol) $^{-1}$, temperature = 437°C, total pressure = 1 atm, toluene/methanol = 5, helium/(toluene + methanol) = 5.

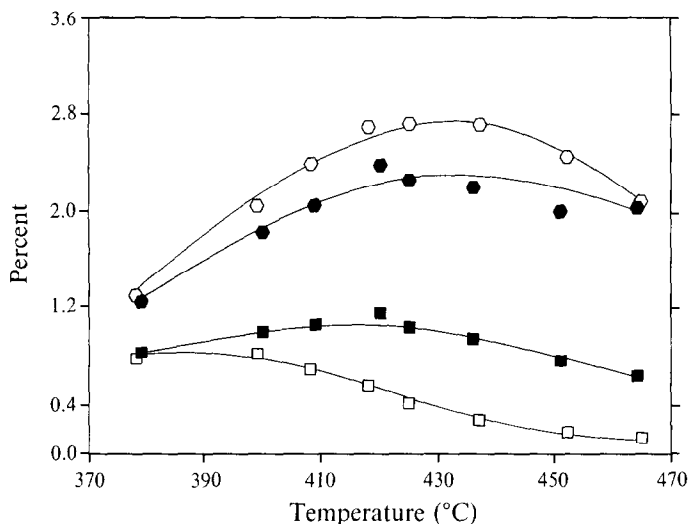


FIG. 4. Temperature dependence on toluene conversion and styrene yield. Toluene conversion: ●, CsAce/CsNaX; ○, CsAce/CsNaY. Styrene yield: ■, CsAce/CsNaX; □, CsAce/CsNaY. $W/F = 1.45 \times 10^{-3}$ mole zeolite unit cell \cdot h \cdot (moles of toluene + methanol) $^{-1}$, total pressure = 1 atm, toluene/methanol = 5, helium/(toluene + methanol) = 5.

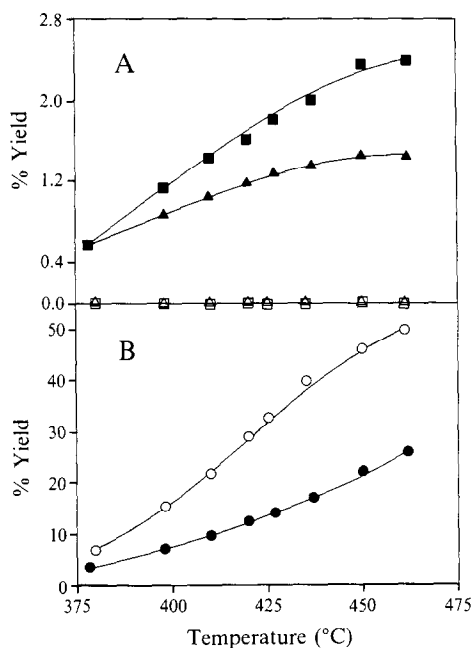


FIG. 5. Influence of temperature on decomposition of methanol. (A) Formaldehyde yield from ▲, CsAce/CsNaX; △, CsAce/CsNaY. DME yield from ■, CsAce/CsNaX; □, CsAce/CsNaY. (B) CO yield from ●, CsAce/CsNaX; ○, CsAce/CsNaY. $W/F = 1.45 \times 10^{-3}$ mole zeolite unit cell \cdot h \cdot (moles of toluene + methanol) $^{-1}$, total pressure = 1 atm, toluene/methanol = 5, helium/(toluene + methanol) = 5.

DME are observed. Figure 5B shows also the yields of CO for CsAce/CsNaY and CsAce/CsNaX. For all temperatures, the yield of CO from CsAce/CsNaY is significantly higher than that obtained from CsAce/CsNaX. CO₂ yields (not shown) are fairly similar for both zeolites and range from ~0.15% at 380°C to ~1.3% at 465°C.

Table 2 lists the conversions of toluene and methanol at 425°C for the impregnated zeolites and MgO. Listed also are the product yields from toluene and methanol. Note that MgO did not convert toluene. Interestingly, MgO and CsAce/CsNaY show similar methanol decomposition products. Only trace formaldehyde and DME are observed over these catalysts and both exhibit high CO formation.

The alkylation of acetone, ethane, and methane with methanol was studied over the impregnated X and Y zeolites at a W/F identical to that used for the alkylation of toluene. Table 3 lists the bond strength of the C-H bond suspected to be activated as well as the conversion of substrate and methanol. No conversion is observed for either methane or ethane. At higher tem-

TABLE 2
Toluene Alkylation with Methanol: Conversions and Yields at 425°C

Catalyst	Reactants		Products						
	% Conversion of toluene	% Conversion of methanol	% Yield of styrene	% Yield of EB	% Yield of xylenes	% Yield of CO	% Yield of CO ₂	% Yield of CH ₂ O	% Yield of DME
CsAce/CsNaX	2.27	33.4	1.07	1.07	0	14.4	0.97	1.28	1.81
CsAce/CsNaY	2.74	54.3	0.43	2.29	0	33.0	0.49	Trace	Trace
MgO	0	32.8	0	0	0	28.0	0.36	Trace	Trace

peratures (e.g., 465°C) ethane and methane remain unreacted.

Alkylation of acetone with methanol was observed over both catalysts at 425°C. However, the majority of the reacted acetone form products which appear to result from acetone aldol condensations.

Table 4 gives the superficial and bulk chemical analyses of cesium and silicon for the CsNaY and CsAce/CsNaY catalysts. Included in Table 4 are analogous data from rhodium-containing zeolite A and zeolite Y catalysts which will be used for comparative purposes (*vide infra*).

DISCUSSION

Acid/Base Properties

In the decomposition of isopropanol to acetone and propylene the acid/base properties are typically based on the rate and selectivity of acetone and propylene pro-

duction. Although some ambiguity can exist as to whether the propylene results from a Brønsted acid site (14, 15) or from the decomposition of an alkoxide intermediate (16–21), the production of acetone is fairly well accepted to result from base sites (16–21). Because activity and selectivity can be strongly influenced by temperature it was necessary to determine whether conclusions obtained at 350°C (1, 2) were valid also at temperatures consistent with those used for the side chain alkylation of toluene with methanol. From Fig. 4 the optimum temperature for toluene conversion ranges between 425 and 435°C for both CsAce/CsNaX and CsAce/CsNaY. This range is within those reported earlier (4, 6). Thus, we performed isopropanol decomposition studies at 425°C. To assess the relative activity of each catalyst, i.e., yield of acetone and propylene, all catalysts were compared at a constant contact time (Fig. 1). The con-

TABLE 3
Substrate Alkylation with Methanol at 425°C

Substrate	C–H acidity ^a (approx. pK _a)	CsAce/CsNaY		CsAce/CsNaX	
		% Conv. substrate	% Conv. methanol	% Conv. substrate	% Conv. methanol
Acetone	20	5.87 ^b	39.1	7.83 ^b	37.2
Toluene	35	2.74	54.3	2.26	33.4
Methane	40	0.0	72.7	0.0	42.4
Ethane	42	0.0	89.9	0.0	53.4

^a From Ref. (31).

^b Yields of methylvinylketone plus methylethylketone were 0.26% and 0.23% for CsAce/CsNaY and CsAce/CsNaX, respectively.

TABLE 4

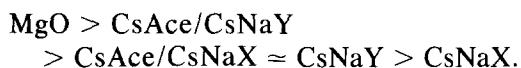
Superficial and Bulk Analyses of Zeolite Catalysts

Catalyst	Loading weight %	Metal/Si		XPS/CA
		CA	XPS	
CsNaY	0.0 Cs ⁺	0.33	0.38	1.15
CsAce/CsNaY	1.95 Cs ⁺	0.37	0.45	1.22
RhNaA ^a	1.25 Rh ³⁺	0.02	1.33	60
RhNaY ^a	2.37 Rh ³⁺	0.023	0.023	1.0

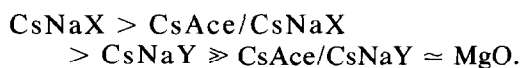
^a From Ref. (29).

versions of isopropanol measured at constant contact time were not differential. Therefore, selectivities could not be compared. However, in a separate set of experiments the catalysts were compared at constant conversion (4.73%) in order to determine the selectivities to acetone and propylene (Fig. 2). From the activity and selectivity data illustrated in Figs. 1 and 2, the acid/base properties of the catalysts can now be assessed.

From Figs. 1 and 2 it appears that the ability of the materials tested here to promote a based mediated reaction follows the order of



Unlike MgO and CsAce/CsNaY (1, 2), the propylene formation from CsNaX, CsNaY, and CsAce/CsNaX appears to result from Brønsted acidity (not reported). Therefore, the acidic character of the materials tested here follows the order of



Alkylation of Toluene with Methanol

Active base sites. Considerable evidence has been reported to suggest that base sites are essential for the side chain alkylation of toluene with methanol. The base sites appear to promote (i) the dehydrogenation of methanol to formaldehyde (4) and (ii) pro-

ton abstraction from the methyl group of toluene to form a reactive carbanion intermediate (22). As illustrated in Figs. 1 and 2, impregnation of the cesium zeolites results in enhanced dehydrogenation activity and selectivity. For zeolites X and Y, the increase in acetone yield and selectivity is paralleled by an increase in toluene conversion, although not proportionately (Fig. 4). Note that the promotion in toluene conversion resulting from occluded exchange salts in CsNaX has been reported elsewhere as well (10, 12). Thus, it appears that a relationship exists between base activity (as defined by acetone production) and the side chain alkylation of toluene. Interestingly, MgO which has been demonstrated here via isopropanol decomposition to possess excellent base activity does not catalyze the alkylation of toluene (Table 2). This too has been reported elsewhere (23) and illustrates that aspects other than active base sites must be important in the side chain alkylation of toluene with methanol.

Microporosity. Several authors have suggested that geometric factors may also play an important role for side chain alkylation. It appears that the replacement of sodium atoms with cesium not only increases the base properties of the zeolite (1, 24, 25) but, as suggested by Unland and Barker (9), serves also to influence the electrostatic forces and geometric constraints within the zeolite pores favoring side chain over ring alkylation. The influence of the cesium cation on toluene adsorption was established further by Sefcik (26), who reported that when toluene was adsorbed into CsNaX and NaX, the rotational frequency (observed by NMR) of toluene located in CsNaX was approximately two orders of magnitude smaller than that recorded for NaX. It was suggested by Sefcik that steric rather than electrostatic forces were responsible for reducing toluene mobility which in turn influences the attack of the methyl group over the aromatic ring. The influence of spatial effects is supported by Garces *et al.* (6), who demonstrated that

cesium salts supported on microporous carbon were just as active for side chain alkylation as CsNaX. It was noted also that carbon supports with larger pores were not as active.

The adsorption of argon at liquid argon temperatures and at $P/P_0 < 10^{-3}$ by molecular sieves is generally attributed to microporous adsorption (27, 28). Argon was not adsorbed on the MgO used here at $P/P_0 < 10^{-3}$ revealing that no microporosity exists (i.e., $< 20 \text{ \AA}$). Thus, the notion that microporosity may play a role in side chain alkylation of toluene is supported here by argon adsorption and the fact that although MgO and CsAce/CsNaY have similar isopropanol and methanol decomposition (vide infra) behavior, toluene conversion is not observed from MgO.

From isopropanol decomposition, CsAce/CsNaY was shown to have considerably more base activity than CsAce/CsNaX (Figs. 1 and 2). Moreover, CsAce/CsNaY is known to possess the microporosity suggested to be necessary to influence toluene adsorption. Therefore, one might expect a significant increase in toluene conversion for CsAce/CsNaY over CsAce/CsNaX. However, such is not the case (Table 2).

One possibility for why the expected enhancement is not observed is that the impregnation of cesium acetate results in extracrystalline rather than intracrystalline cesium. Thus, newly formed base sites generated from the decomposition products of cesium acetate would not be in a microporous environment. To determine the location of the decomposition products, superficial-to-bulk analyses were performed. Two samples were prepared. One was CsNaY which was rinsed with 0.01 N cesium acetate after exchange to remove the possibility of any occluded exchange salt yet minimize decationation. The other was CsNaY impregnated by the procedure discussed above at 2.8 wt%. Both samples were calcined in helium at 450°C and submitted for superficial (XPS) and bulk chemical (CA) analyses of silicon and cesium. From

Table 4 the superficial-to-bulk ratios (i.e., XPS/CA ratio) were fairly close to unity at 1.15 and 1.22 for the untreated and impregnated CsNaY zeolite, respectively, suggesting that the cesium is well dispersed for both samples. Interestingly, Shannon *et al.* (29) reported superficial-to-bulk analyses from zeolites to determine whether rhodium was exchanged into the zeolites or remained on the extracrystalline surface after filtration. As evidenced in Table 4, the superficial-to-bulk ratios for zeolite A (1.25 wt% Rh³⁺) and Y (2.37 wt% Rh³⁺) were 60 and 1, respectively. These results indicate that rhodium does not exchange into zeolite A (remains extracrystalline) but does into zeolite Y. However, what is more important to this study, the results demonstrate how small surface coverages (1.25 wt% Rh³⁺) can strongly influence superficial-to-bulk atomic ratios. Thus our superficial-to-bulk data suggest that the decomposition products of cesium acetate are in fact intracrystalline. Therefore, the lower than expected activity of CsAce/CsNaY appears not to involve the absence of the cesium acetate decomposition products in a microporous environment.

Stabilization of formaldehyde. Several authors have suggested that acid sites (Lewis and/or Brønsted) may interact with the pi electrons of the toluene ring to influence the adsorption of toluene and perhaps increase the acidity of the methyl protons (9, 13). It has been suggested also that acid sites may aid in stabilizing formaldehyde and thus suppress its decomposition to CO and H₂. Unland and Barker (9) demonstrated with infrared spectroscopy that the occlusion of boric acid (most likely in the form of B₂O₃) into the zeolite pores has no apparent influence on the adsorbed toluene yet significantly influences the adsorption of formaldehyde. They concluded that the boron may slow the decomposition of formaldehyde by either (i) providing acidity in the area around the active base sites or (ii) neutralizing strong base sites which may otherwise promote the decomposition of

formaldehyde to CO and H₂. These results were supported further by Itoh *et al.* (13) who demonstrated using quantum chemical calculations that formaldehyde is far more stable when interacting with an acid site (e.g., H⁺) than with a base site (e.g., OH⁻).

From the work of Unland and Barker and Itoh *et al.*, it appears that the decomposition of formaldehyde can be slowed by either direct interaction with available acid sites or neutralization of strong base sites. Noller and Ritter (21) studied the decomposition of methanol over magnesia-silica mixed oxides (i.e., mixtures ranging in composition from 100% SiO₂ to 100% MgO). Acid titration studies using 4-dimethylaminoazobenzene ($pK_a = 3.3$) suggested that the high silica (10 mol% MgO) and high magnesia (70 mol% MgO) samples had similar acid densities. However, in contrast to the high silica sample, no formaldehyde was observed over the more basic, high magnesia sample. These results may suggest that the rate of formaldehyde decomposition is more strongly influenced by the presence of strong base sites than by the presence of strong acid sites.

In Fig. 5A, DME and formaldehyde yields during toluene alkylation are shown for both the CsAce/CsNaX and CsAce/CsNaY zeolites as a function of the reaction temperature. For the CsAce/CsNaX zeolite both formaldehyde and DME are observed in the product stream while only trace formaldehyde and DME are observed for CsAce/CsNaY. Furthermore, note that the absence of formaldehyde from CsAce/CsNaY (Fig. 5A) is accompanied by a high yield of CO as illustrated in Fig. 5B. From the isopropanol decomposition studies (Fig. 1 and Ref. (2)), CsAce/CsNaY showed virtually no Brønsted acidity and very high base activity, neither of which was suggested to aid in suppressing the rate of formaldehyde decomposition. Moreover, MgO, which possesses virtually no Brønsted acidity and high base activity (1, 2) shows (in agreement with Noller and Ritter) only trace formaldehyde and high

CO production as well (Table 2). Therefore, the lower than expected toluene conversions observed for CsAce/CsNaY could result from the rapid decomposition of formaldehyde, i.e., the suggested alkylating agent (4).

The formation of DME from CsAce/CsNaX could be explained by (i) the acidity of the CsAce/CsNaX (demonstrated by isopropanol decomposition to propylene) which may result in an acid catalyzed reaction of methanol to form DME and/or (ii) the reaction of formaldehyde to DME as suggested by Venuto and Landis (30). CsAce/CsNaX possesses moderate base activity and Brønsted acidity (from isopropanol decomposition studies) both of which were suggested to aid in suppressing the decomposition of formaldehyde. Interestingly, Fig. 5A shows formaldehyde in the product stream of CsAce/CsNaX.

Alkylation of Other Substrates with Methanol

As discussed above, the deprotonation of the organic substrate to form a carbanion intermediate has been suggested as a key step in the mechanism of side chain alkylation (22). Therefore, it was of interest to establish how substrate acidity influences substrate conversion. From this, reaction diversity can be better assessed. The pK_a values reported for acetone, toluene, methane, and ethane are 20, 35, 40, and 42, respectively (31). Note that the pK_a of ethane and methane are only approximate (31). From these values one might expect the order in substrate conversion to follow acetone > toluene ≫ methane ≈ ethane. From Table 3, it is shown that neither ethane or methane was alkylated. Higher temperature, e.g., 460°C, did not promote alkylation as well. A report on the alkylation of acetone over Fe³⁺/MgO (32) suggested that acetone could be alkylated with methanol to methylvinylketone over the impregnated zeolites. From Table 3, acetone was alkylated over both zeolites; however, the majority of the reacted acetone appeared to

form aldol condensation products. Interestingly, the substrate conversions are directly related to the C-H acidity.

In summary, it has been demonstrated that an increase in base character promotes side chain alkylation yet at the expense of formaldehyde decomposition. Thus, to increase side chain alkylation it appears that either formaldehyde must be stabilized (as attempted by previous authors) or because of the apparent need for geometric/electron factors, alternate pore structures must be explored.

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