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Solid base catalysts for side-chain alkylation of toluene with methanol

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Abstract

A wide variety of solid bases, including alkali-exchanged zeolites X, Y, L and β, and alkali-impregnated carbon and magnesia, were tested as catalysts for the side-chain alkylation of toluene with methanol to form styrene and ethylbenzene. In addition, the effects of adding Group IIIA elements (B, Al, Ga, In) to the catalysts were examined. At 680 K and atmospheric pressure, the major reaction products were styrene, ethylbenzene, and carbon monoxide. Cesium-exchanged zeolite X was the most effective alkali-containing catalyst for the alkylation reaction. Of the Group IIIA additives that were tested, only boron promoted the alkylation reaction. The primary effect of adding boron was to reduce the decomposition of methanol to carbon monoxide. Apparently, boron selectively modifies the sites associated with methanol decomposition without inhibiting the sites active for alkylation. A borated Cs–carbon sample also catalyzed the alkylation reaction, demonstrating that a zeolite framework is not necessary to form the active site. Microporosity seems to play an important role in these catalysts since both the alkali-modified carbons and the zeolites are microporous.

Keywords: Toluene; Methanol; Styrene; Ethylbenzene; Zeolite; Carbon; Magnesia; Boron; Alkali; Potassium; Rubidium; Cesium

1. Introduction

Relatively little is known about the chemistry of base-catalyzed reactions on solid metal oxides and zeolites compared to the analogous acid-catalyzed reactions. For example, the reaction of methanol with toluene over acidic zeolites leads to alkylation of the aromatic ring to produce xylenes [1–3]. The chemistry is well known and the selectivity for the *para* isomer of xylene can be altered by adjusting the pore size of the zeolite catalyst. However, the side-chain alkylation of toluene with methanol over solid bases is much less understood. Alkali-containing zeolites have been reported to catalyze the toluene alkylation reaction with methanol to form styrene and ethylbenzene with modest yields and selectivities [4–15]. Other solid bases like MgO, MgO–TiO_2 and CaO–TiO_2 [16] catalyze the alkylation reaction but are not as effective as the basic zeolites. One system, however, composed of a cesium-containing microporous carbon, promoted with boron, catalyzed the reaction with activity and selectivity similar to a Cs–zeolite catalyst [11].

It is generally believed that the side-chain alkylation of toluene takes place in the microporous voids of the catalyst through multiple steps. Methanol is first dehydrogenated catalytically to produce formaldehyde, which is the

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likely alkylating species since earlier experimental and quantum-mechanical studies have demonstrated that it is an effective reactant for toluene alkylation over basic zeolites [6,12]. Next, the alkyl group of toluene is activated by adsorption onto a basic site. Finally, the alkylation of toluene with formaldehyde forms styrene and water. Most researchers report that significant quantities of ethylbenzene are also produced over basic zeolites from the subsequent hydrogenation of styrene. The major undesirable side reaction is the decomposition of methanol to carbon monoxide, presumably through a formaldehyde intermediate.

According to the above mechanism, a catalyst must expose basic sites strong enough to activate the methyl group of toluene; however, very strong solid bases are also good catalysts for decomposing methanol to carbon monoxide. Earlier studies have investigated several methods for modifying the catalytic activity of basic zeolites for toluene alkylation, including variation of the Si/Al ratio of the zeolite [4,12] and the use of additives such as occluded alkali salts [4], alkali hydroxides [13], and elements like B, P, Cu and Ag [14,15]. In the present study, we evaluated the effects of zeolite type (X, Y, L, β), alkali cation (Na, K, Rb, Cs), addition of occluded alkali (K, Cs) oxides, addition of Group IIIA elements (B, Al, Ga, In), and use of non-zeolitic supports (carbon, magnesia) in order to better understand the critical parameters that influence the toluene alkylation reaction over solid bases.

2. Experimental methods

2.1. Materials synthesis

Zeolites NaX, NaY and KL were obtained from Union Carbide, and zeolite Naβ was obtained from PQ Corp. Cesium and rubidium zeolites were prepared from these starting materials by three ion exchanges with 1 M aqueous solutions of the appropriate acetates followed by a final wash in dilute aqueous alkali hydroxide solution at a pH of 13. A Cs-exchanged zeolite β sample was synthesized by Dow Chemical Co. according to the method described above. Potassium-exchanged zeolites were also synthesized by the same method except that nitrate was used in the exchange solution instead of acetate and the exchanged samples were calcined in air at 783 K for 2 h before rehydrating and rinsing with alkali hydroxide.

Microporous carbon (Armak, micropore volume = 0.396 $cm^3\ g^{-1}$ determined from N_2 adsorption) and magnesia (Ube Industries) were impregnated with aqueous solutions of alkali acetates to the point of incipient wetness and dried in air. The nominal weight loadings of the alkalis were 3.9, 8.6 and 13 wt.-% for KC, RbC and CsC, respectively, and 30 wt.-% for Cs–MgO.

Group IIIA elements were also added to some catalysts by aqueous impregnation with H_3BO_3, $Al(NO_3)_3$, $Ga(NO_3)_3$ and $In(NO_3)_3$.

Elemental analyses were performed by Galbraith Laboratory, Inc. (Knoxville, TN). Argon adsorption isotherms at 87 K were recorded on an Omnisorp 100CX (Coulter Corp.) and micropore volumes were calculated from the uptake of argon at a relative pressure of 0.3.

2.2. Catalytic reaction

Catalyst powders were pressed, crushed and sieved to −40/+60 mesh, loaded into a single pass fixed bed reactor, and heated in situ at 783 K in flowing He (99.99% Roberts Oxygen) for 2 h before cooling to the reaction temperature of 680 K. A liquid mixture of toluene (Aldrich, 99.8%) and methanol (Fisher, reagent grade) at a 5:1 molar ratio was then pumped into the reactor system at a rate of 2.0 $cm^3\ h^{-1}$ (liquid). These reactants were vaporized and then mixed with flowing He in a 5:1 molar ratio of He to organics before entering the catalyst bed. For zeolite X and Y catalysts, the mass of zeolite loaded into the reactor was chosen to give a constant reactor space time based on zeolite unit cells and reactant flow rates. We chose W/F to be about 1.4×10^{-3} mol zeolite unit cell · h · (mol organic feed)$^{-1}$. For the carbon samples, the molar loading of the alkali into the reactor was similar to the alkali loading for zeolite X. For catalysts other than zeolites X and Y, the corresponding W/F values are included with the results. Exit gases were analyzed by a gas chromatograph equipped with an HP1 fused silica capillary column for the heavy products and a Haysep Q packed column for the light gases.

The reactivity results are presented as methanol conversion, aromatic yield and aromatic selectivity, which are defined as follows (quantities are molar flowrates):

methanol conversion
$= 1 - (\mathrm{MeOH}_{\mathrm{exit}})/(\mathrm{MeOH}_{\mathrm{feed}})$
aromatic yield $= (\mathrm{S} + \mathrm{EB})/(\mathrm{MeOH}_{\mathrm{feed}})$
aromatic selectivity
$= (\mathrm{S} + \mathrm{EB})/(\mathrm{S} + \mathrm{EB} + \mathrm{CO} + \mathrm{CO}_2)$

where MeOH, S and EB represent methanol, styrene and ethylbenzene, respectively. For all of the materials tested, the major non-aromatic product detected was carbon monoxide. However, the methanol material balance did not close satisfactorily when the carbon catalysts were used. In all other cases, the methanol material balance closed within 5%. We suspect that the undetected product is most likely formaldehyde that reacts in the gas chromatograph, since the post-reaction weights of the catalysts did not indicate that products were depositing on the catalysts in substantial amounts. Subsequent blank tests with solutions of formaldehyde in water and methanol indicated that our gas chromatograph system cannot quantitatively assess the formaldehyde concentration in the product stream. The reactivity results listed in Table 6 for the alkali-modified carbons illustrate this point.

3. Results and discussion

The results from elemental analysis shown in Table 1 indicate that fairly high levels of ion exchange were achieved with zeolites X and Y. Also, the percent of sodium-exchanged decreased with increasing alkali ion size, which is the expected trend based on the ion-exchange isotherms [17]. Table 2 summarizes the micropore volumes of the zeolites determined from argon adsorption isotherms. As expected, the pore volume decreased with increasing cation size. Since the larger alkali ions contribute a greater fraction to the total weight of the sample, we also show in Table 2 the micropore volumes of the zeolites normalized to the weights of the aluminosilicate framework, thus removing the effect of the different alkali weights. The decrease in pore volume with increasing alkali ion size, as calculated in the third column, demonstrates conclusively that the larger ions occupy a greater fraction of the intrazeolitic void space than the smaller ions. These results from elemental analysis and argon adsorption verify that ion-exchanged zeolites X and Y were prepared.

Table 1
Elemental analyses of alkali-exchanged zeolites X and Y

Catalyst	Composition	%Na exchanged	Si/Al [a]
NaX	$Na_{78.8}Si_{104}Al_{87.7}O_{384}$	–	1.19
KX	$K_{66.7}Na_{13.6}Si_{104}Al_{87.7}O_{384}$	83.1	1.19
RbX	$Rb_{60.4}Na_{28.5}Si_{104}Al_{87.7}O_{384}$	68.9	1.19
CsX	$Cs_{46.8}Na_{33.6}Si_{104}Al_{87.7}O_{384}$	58.2	1.19
NaY	$Na_{53.7}Si_{138}Al_{54.1}O_{384}$	–	2.55
KY	$K_{48.6}Na_{4.56}Si_{138}Al_{54.1}O_{384}$	91.4	2.55
CsY	$Cs_{50.2}Na_{8.81}Si_{138}Al_{54.1}O_{384}$	85.1	2.55

[a] Based on the Si/Al ratio of NaX or NaY.

Reactivity results for alkali-exchanged X and Y zeolites are given in Tables 3 and 4, respec-

Table 2
Micropore volumes of alkali-exchanged zeolites X and Y

Catalyst	Pore volume/ cm^3 Ar (g)$^{-1}$	Pore volume/cm^3 Ar (g zeolite framework [a])$^{-1}$
NaX	0.239	0.277
KX	0.199	0.250
RbX	0.162	0.237
CsX	0.122	0.198
NaY	0.254	0.281
CsY	0.102	0.163

[a] Zeolite framework consists of silicon and aluminum oxides.

Table 3
Effect of occluded alkali metal oxides on toluene alkylation reactivity

Catalyst	Methanol conversion/%	Aromatic yield/%	Aromatic selectivity/%	S/(S + EB)/%
NaX [a]	45	3.3	7.3	33
KX	72	16	22	34
KX: 5% KNO_3	55	5.8	11	33
KX: 10% KNO_3	94	4.9	5.2	11
KX: 15% KNO_3	83	3.3	4.0	12
CsX	45	15	32	22
CsX: 5% CsAce	84	15	17	5.1
CsX: 10% CsAce	76	12	15	16
CsX: 15% CsAce	48	6.3	13	13

[a] Trace amounts of xylenes and dimethyl ether were produced but are not accounted for in the table.

Table 4
Toluene alkylation over alkali-exchanged zeolite Y

Catalyst	Methanol conversion/%	Aromatic yield/%	Aromatic selectivity/%	S/(S + EB)/%
NaY [a]	5.1	trace	trace	–
KY	23	3.0	13	65
CsY	64	11	19	59

tively. In addition to ethylbenzene and styrene, the NaX and NaY catalysts produced xylenes, indicating that some acidity is associated with the samples. Ion exchange with heavier alkalis, followed by a hydroxide wash, reduced the acidity since no xylenes were produced over the other zeolites. The results in Tables 3 and 4 show that alkali-exchanged X zeolites are more effective catalysts for side-chain alkylation than the analogous Y zeolites. Hathaway and Davis

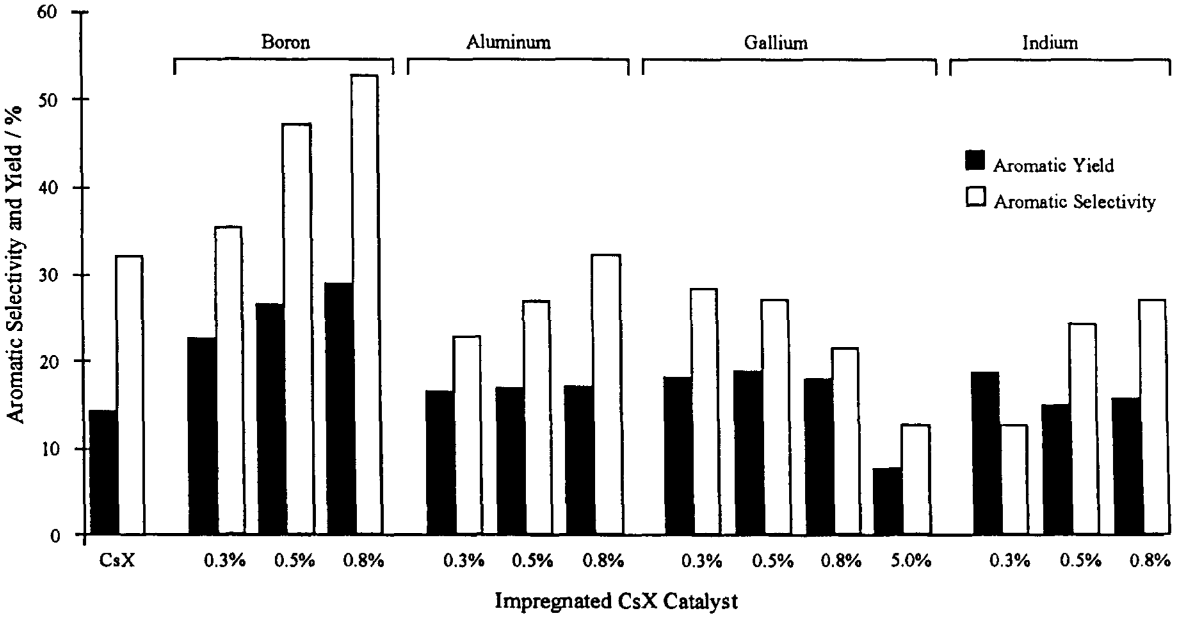

Fig. 1. Effect of Group IIIA elements on alkylation catalysis by CsX zeolite. The amount of added IIIA element is expressed in nominal weight percent.

reported that impregnating alkali ions into the pores of X and Y zeolites promoted the toluene alkylation reaction [4]. Since the alkali content was greater than the ion-exchange capacity, the alkali ions were most likely present in metal oxide clusters supported inside the zeolite cages. Subsequent characterization and reactivity studies with occluded cesium in zeolite Y indicate that the extraframework moieties are probably Cs_2O clusters [18,19]. In our work, the yields and selectivities of exchanged and hydroxide-washed CsX compare very well with those of the Cs-impregnated samples of Hathaway and Davis. We also incorporated additional alkali oxide clusters into our zeolite X samples in an attempt to improve the alkylation activity of our most effective catalysts. As shown in Table 3, impregnation of KX and CsX with nitrate and acetate salts, respectively, followed by decomposition, did not yield more active or selective catalysts. In fact, the high conversion of methanol achieved with these materials resulted mostly from non-selective decomposition to carbon monoxide. The unique features associated with alkali-exchanged zeolites containing a small excess of alkali are eliminated by incorporating greater amounts of occluded oxides, presumably due to the high base strength of the alkali oxides.

Earlier reports suggest that boron is an effective promoter for the base-catalyzed alkylation of toluene with methanol [15,20]. In the current work, we examined the effects on aromatic yield and selectivity of adding B, Al, Ga and In to a CsX catalyst, and the results are shown in Fig. 1. Only boron promoted aromatic yield and selectivity. Although the nominal weight percent of each element is shown in Fig. 1, the 5 wt.-% Ga sample contains a similar molar amount of additive as the 0.8 wt.-% B sample. Thus, based on both equivalent weight or mole percents, only boron promotes the reaction. Since boron was impregnated in the form of boric acid, whereas the other Group IIIA elements were impregnated as nitrates, one may suspect that the acidity of the boron precursor was the important factor for promotion. However, Unland and Barker have presented evidence from infrared spectroscopy that boric acid in these materials dehydrates at the reaction temperature, most likely to form boron oxide [15]. In addition, impregnation of alkali zeolites with cesium borate also results in more effective catalysts than the original materials [10]. Apparently, boron modifies the active sites for the reaction in a unique manner.

Both the aromatic selectivity and the S/(EB + S) ratio increased following the addition of boron to all of our alkali-exchanged zeolite X catalysts as shown in Table 5. Styrene is believed to be the primary alkylation product which may undergo subsequent hydrogenation to ethylbenzene. Garces et al. concluded that the hydrogen is derived from methanol rather than dihydrogen since H_2 was not an effective hydrogenating agent for styrene over alkali-containing zeolite and carbon [11]. Evidently, the decomposition of methanol to formaldehyde and hydrogen atoms yields a catalyst surface with a high virtual pressure or fugacity of dihydrogen.

Table 5
Toluene alkylation over boron-impregnated zeolite X catalysts [a]

Catalyst	Methanol conversion/%	Aromatic yield/%	Aromatic selectivity/%	S/(S + EB)/%
KX	72	16	22	34
KX + B	10	4.6	46	88
RbX	77	15	20	17
RbX + B	47	16	34	22
CsX	45	15	32	22
CsX + B	56	27	47	24

[a] 0.5 wt% (nominal) boron loading.

Table 6
Toluene alkylation over boron-impregnated carbon catalysts [a]

Catalysts	W/F/g h (mol organic)$^{-1}$	Methanol conversion/%	Aromatic yield/%	Aromatic selectivity/%	S/(S + EB)/%
C [b]	26	0.0	0.0	0.0	–
KC	22	21	0.4	6.0	0.0
KC + B	23	9.8	0.5	100	0.0
RbC	26	18	1.9	16	0.0
RbC + B	25	20	2.4	18	0.0
CsC	21	54	3.0	7	0.0
CsC + B	24	50	4.3	15	0.0

[a] 0.5 wt.% (nominal) boron loading.
[b] As received microporous carbon.

Since carbon monoxide formation also liberates hydrogen atoms from the reaction intermediate formaldehyde, inhibition of CO formation should lower the dihydrogen virtual pressure and therefore retard the rate of styrene hydrogenation. Indeed, both the S/(S + EB) ratio increased and the CO formation rate decreased with boron incorporation into alkali-exchanged X zeolites. Apparently, B_2O_3 may selectively poison some of the strongly basic sites that catalyze the dehydrogenation of intermediate formaldehyde to carbon monoxide. This hypothesis is consistent with earlier speculations by Unland and Barker on the role of boron [15].

Alkali-loaded microporous carbons also catalyze the side-chain alkylation of toluene with methanol as shown in Table 6. Adding 0.5 wt.-% boron to the alkali-modified carbons increased the aromatic yields and selectivities of RbC and CsC by decreasing the rate of methanol decomposition to carbon monoxide. Minimal alkylation activity was observed for potassium-loaded carbon, with or without added boron. Ethylbenzene was the only aromatic product formed over the modified carbon catalysts.

Other zeolitic (L, β) and non-zeolitic (MgO) supports for alkalis were also tested for alkylation activity. The results in Table 7 show that none of these materials are effective catalysts for alkylation.

The nature of the active sites for side-chain alkylation of toluene with methanol is still unresolved. Results from our study and others confirm that CsX zeolites promoted with boron are among the most effective catalysts for the reaction. In these materials, there are at least two different oxide sites that can function as base sites: the oxygen atoms of the zeolite framework and the oxygen atoms in occluded alkali oxides (and hydroxides). The average partial negative charge associated with a framework oxygen atom can be estimated from the average Sanderson electronegativities of the zeolites [21] and can be used to rank the materials according to basicity. Accordingly, the average partial charges of a framework oxygen in CsX and an oxygen in Cs_2O are -0.45 and -0.94, respectively. The greater negative charge associated with oxygen atoms in the alkali oxide is consistent with the high basicity of these materials

Table 7
Toluene alkylation over alkali-modified magnesia and zeolites L and β

Catalyst	W/F/g h (mol organic)$^{-1}$	Methanol conversion/%	Aromatic yield/%	Aromatic Selectivity/%
Cs–MgO	23	6.8	0.0	0.0
CsL	29	48	0.6	1.2
Csβ	21	8.4	0.0	0.0

compared to zeolites. In fact, titration experiments have shown that Rb_2O and Cs_2O are 'superbases' [22], which are defined as materials possessing basic sites stronger than $H_- = -26$ [23]. Alkali oxides occluded in the pores of zeolites reportedly catalyze olefin cracking [24], propanol dehydrogenation [4] and butene isomerization [18,19]. However, zeolites containing a large number of these superbasic oxide clusters are likely to be too basic for the toluene reaction since methanol decomposition to carbon monoxide will compete with alkylation. Our results in Table 3 confirm that occluded alkali oxides in KX and CsX produce large quantities of CO thus lowering the selectivity and yield of the alkylation reaction. Similarly, K, Rb and Cs oxide-loaded carbon catalysts produced mostly carbon monoxide instead of alkylation products, as shown in Table 6.

The chemical states of the alkali metal and/or alkali oxide clusters under reaction conditions are unknown at this time. Garces et al. presented evidence that, at temperatures near those used for toluene alkylation, alkali metal vapors, metal oxides, suboxides, and carbonates are present in the reactor [11]. They speculate that these species generated in situ form the basic sites necessary for side chain alkylation of toluene with methanol. However, subsequent studies with cesium oxides occluded in zeolite Y indicate that Cs_2O remains intact even after treatment at temperatures high enough to decompose bulk Cs_2O [18]. Analogous clusters synthesized on a carbon support are suspected of transforming into cesium suboxides under similar conditions [18]. The reason for the stabilization of alkali oxide clusters in zeolites is not clear [18].

The unique chemical environment in borated CsX may indicate that zeolite framework oxygen atoms are necessary for the alkylation reaction. However, as shown previously by Garces et al. [11] and repeated by us, borated Cs–carbon is also an effective alkylation catalyst which demonstrates that zeolite framework oxygen atoms are not a necessary condition for alkylation activity. Both materials are microporous, suggesting that a restricted environment in the vicinity of the basic sites may be needed to enhance the reactivity [4,6,11]. Further supporting this theory, a non-microporous MgO impregnated with Cs was not active for the reaction. We also tested the dimensionality of the zeolite framework on alkylation activity. Zeolites X and Y possess three dimensional pore networks which allow easy access of the reactant molecules to the intracrystalline basic sites. A Csβ catalyst, which possesses a two dimensional channel structure, was not effective for the alkylation reaction. Cesium-exchanged L zeolite, which has unidimensional pores, was also minimally active for the alkylation reaction. However, the L zeolite decomposed substantial amounts of methanol to CO. We suspect that the unidimensional pore network of zeolite L increases the residence time of methanol in the zeolite crystals longer than zeolites with pore networks of higher dimensionality, thus increasing the likelihood of methanol decomposition.

4. Note added in proof

Further characterization of the β and L zeolite catalysts indicated that our method of Cs incorporation caused severe loss in pore volume.

5. Conclusions

A borated CsX zeolite was the most effective catalyst tested in this work for side-chain alkylation of toluene from methanol. Comparisons of the yield and selectivity of CsX + B to results from other alkali-containing catalysts leads to the following conclusions. Catalysts possessing extremely strong basicity, or superbasicity, are not effective for alkylation due to excessive decomposition of methanol to carbon monoxide. Non-zeolitic supports like microporous carbon catalyze the alkylation reaction when they are modified with alkali and boron. Although the carbon-based catalysts were not quite as effective as CsX + B in this study, the results indicate that solids other than zeolites are potential side-chain alkylation catalysts.

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