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Role of Acid and Base Sites in the Side-Chain Alkylation of Alkylbenzenes with Methanol on Two-Ion-Exchanged Zeolites

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The role of acid and base sites in the side-chain alkylation has been investigated using *p*-xylene as alkylbenzene on single- and two-ion-exchanged zeolites. Rb and Li two-ion-exchanged X type zeolites with the Li/Rb+Li ratio of about 0.1 showed a higher activity than RbX and KX which showed the highest activity in single-ion-exchanged zeolites. RbX with a small amount of Li ion has slightly stronger acid sites than RbX, as measured by the temperature-programmed desorption (TPD) of ammonia and the Hammett indicators. Two cations in a zeolite are considered to form different active sites, such as acid and base sites, under their mutual effect. It is concluded that the active center which is the assemblage of acid and base sites with cooperative action is necessary in the side-chain alkylation of alkylbenzenes with methanol.

INTRODUCTION

The side-chain alkylation of toluene with methanol can produce styrene and ethylbenzene without the use of ethylene. This process has been said to be economically attractive (*1*). Furthermore, this reaction is regarded as one of the synthetic methods for the conversion of methyl groups into vinyl and/or ethyl groups. Application of the side-chain alkylation to many alkylbenzenes other than toluene would result in the introduction of vinyl and/or ethyl substituents into the benzene ring with any substituent.

It has been shown that the side-chain and benzene-ring alkylations proceed on the base and acid catalysts, respectively (*2–8*), and they depend linearly on the respective basicity and acidity of the catalysts (*3, 6*). However, by using quantum chemical calculations, it has been suggested in the previous paper (*9*) that the following cooperative action of acid and base sites is very important in the side-chain alkylation: the base site activates the carbon atom of the side chain of toluene and the acid site adsorbs and stabilizes toluene. Here, the role of the acid site in the base catalysts has been pointed out, but it has not yet been confirmed experimentally.

In heterogeneous catalysts, the coexistence of acid and base sites on the catalyst surface has been observed, e.g., alumina which is one of the solid acids contains intrinsic base sites as well as acid sites, and magnesium oxide which is one of the solid bases has some acidity (*10*). Moreover, Hall *et al.* have suggested the structure model of acid and base sites on decationated zeolites (*11*) and Swabb and Gates have proposed the mechanism assuming the coexistence of acid and base sites on H-mordenite (*12*). In the case of zeolites, as the exchangeable cations, such as alkali, alkali earth, and rare earth ions, exist alone as a cation or a hydrated cation, it is considered that the characteristics of each exchanged cation reflect the active site. In particular, alkali ion-exchanged zeolites behave as base catalysts (*3*), reflecting the base character of alkali metals. If two kinds of cations exist in a zeolite, it would be expected that different active sites are formed. This has led to the design of catalysts for the side-chain alkylation. Recently, we reported that the RbX catalyst containing a small amount of Li ions as acid

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ions shows higher activity than RbX for the side-chain alkylation of *p*-xylene (*13*), and this supports the hypothesis of the cooperative action of acid and base sites suggested by quantum chemical calculations (*9*).

It seems to be difficult, however, to examine the role of acid sites in base catalysts such as alkali ion-exchanged zeolites, if their acid sites are very weak. In practice, no acidity is observed by ir spectra of adsorbed pyridine (*14*), although these base zeolites certainly have acid properties considering that the decomposition of 2-propanol yields propene (*15*). If a reactant interacts much stronger with an acid site, the role of weak acid sites could be examined more easily. In other words, the use of a more basic alkylbenzene as a reactant results in a stronger interaction of the reactant and acid site, and this stronger interaction would, in turn, result in the enhancement of the role of weak acid sites for the side-chain alkylation. As *p*-xylene is more basic than toluene because of the electron-donor character of the methyl groups, it is considered that *p*-xylene is superior to toluene as an alkylbenzene to examine the effect of weak acid sites.

In this study, the role of acid sites in the side-chain alkylation of alkylbenzenes with methanol is examined and the active sites formed by some kinds of cations are investigated by preparing the two-ion-exchanged zeolites.

EXPERIMENTAL

Materials and catalysts. Methanol having a purity of 99.5% was obtained from Kishida Chemical Co., Ltd. and was used without further purification. *p*-Xylene was obtained from Showa Denko k.k. and used after purifying it by a silica gel column calcined at 523 K for 2.5 h.

Linde 13X(NaX), SK-40(NaY), SK-45 (NaKL), and Zeolon 100Na(NaM) were used as starting materials of X, Y, L, and mordenite types of zeolites. Each zeolite was pelleted without a binder, crushed, and sized to 28–48 mesh before ion exchange.

Single-ion-exchanged zeolites are zeolites in which only one new cation is incorporated into a starting zeolite by a conventional ion-exchange procedure. Alkali ion-exchanged X and Y, and Mg, Ca, Mn, and La ion-exchanged X belong to this category. These single-ion-exchanged zeolites were prepared by the following method. Six grams of each starting zeolite was placed in a 100-ml beaker and was ion-exchanged 10 times with 50–100 ml of a 0.5–1 *N* aqueous solution of an appropriate chloride at 353 K for 0.5–1 h.

Two-ion-exchanged zeolites are zeolites in which two new cations are incorporated into a starting zeolite. KLiX, RbKX, RbLiX, RbMgX, RbCaX, CsKX, CsLiX, and a series of RbLiX(x) belong to this category. These two-ion-exchanged zeolites, except for a series of RbLiX(x), were prepared by the following method. First, the second cation in the catalyst symbol, for example Li for KLiX, was incorporated by the same procedure used for the preparation of single-ion-exchanged zeolites. Second, the single-ion-exchanged zeolite thus prepared was ion-exchanged with the first cation in the catalyst symbol, for example K ion for KLiX, by the same procedure. Consequently, the zeolite prepared by these processes have two new cations. A series of RbLiX(x) catalysts were prepared by the procedure in which two new cations, that is, Rb and Li, were incorporated simultaneously using an aqueous solution of a mixture of RbCl and LiCl with a molar ratio of x (Rb/Li).

All ion-exchanged zeolites were washed with deionized water until no Cl^- ion was observed in the effluent, and dried at 378 K overnight. The alkali and Mg ion concentrations were determined by atomic absorption spectrophotometry. The other multivalent cation concentrations were calculated from that of the residual sodium ions. The cation compositions of all catalysts are summarized in Table 1.

Apparatus and procedure. The experiments were carried out with a fixed-bed

TABLE 1

Degree of Cation Exchange[a] of Various Catalysts

	Li (%)	Na (%)	K (%)	Rb (%)	Cs (%)	Other cation (%)
LiX	71	22				
NaX		100				
KX			100			
RbX		26		64		
CsX		37			53	
KY			100			
RbY		21		52		
CsY		30			70	
KL			100			
KM			100			
RbKX		17	13	68		
CsKX		15	18		52	
KLiX	0.2	4	49			
RbLiX	2	12		42		
CsLiX	13	12			34	
RbLiX (1)[b]	23	24		39		
RbLiX (2)	15	25		49		
RbLiX (3)	12	23		46		
RbLiX (4)	8	26		46		
RbMgX		22		52		23 (Mg)
RbCaX		4		43		40 (Ca)
MgX		17				40 (Mg)
CaX		6				94 (Ca)
MnX		20				80 (Mn)
LaX		11				89 (La)

[a] Equivalent $Me^{n+}/(AlO_4)^-$.

[b] The values in parentheses represent the molar ratios of RbCl to LiCl in the exchange solution.

flow reactor at atmospheric pressure. All the catalysts were activated by calcination in a flow of nitrogen gas at 773 K for 1 h and brought to the reaction temperature *in situ*. A mixture of *p*-xylene and methanol was fed to the vaporizer using a microfeeder and the vapor of the reactants was carried to the catalyst bed after mixing with the carrier gas. The effluents from the reactor were cooled and periodically collected with an ice trap and a dry ice/ethanol trap. The collected liquid products were analyzed by gas chromatography. Before trapping the effluents, light weight products, such as formaldehyde, CO, CH_4, dimethyl ether, and methanol, were collected with a heated syringe, and were also analyzed by gas chromatography.

The yields of products based on the fed methanol were defined by the same manner as described previously (*9*).

Analysis. The reaction mixture was analyzed by gas chromatography using the following four columns: a 4-mm × 4-m stainless-steel column with Benton 34(7wt%) and DNP(5wt%) on Celite 545 for the liquid products, such as toluene, xylenes, methylstyrene, ethyltoluene, and trimethylbenzenes, at 383 K; a 4-mm × 4-m stainless-steel column with sucrose octaacetate(15wt%) on Daiflon for formaldehyde, dimethyl ether, and methanol at 345 K; a 4-mm × 0.5-m Porapak Q column for CO_2 and dimethyl ether at room temperature; and a 4-mm × 2-m molecular sieve 13X column for H_2, CH_4, and CO at room temperature.

Measurement of acid property of catalysts. The maximum acid strength of the catalysts was measured by using the following Hammett indicators: dicinnamalacetone ($pK_a = -3.0$), 4-benzeneazodiphenylamine($+1.5$), *p*-dimethylaminoazobenzene($+3.3$), 4-benzeneazo-1-naphthylamine($+4.0$), and Methyl Red($+4.8$).

The amount and strength of acid sites were determined by the temperature-programmed desorption(TPD) of ammonia (*16*). The TPD method was carried out using conventional TPD apparatus (*17*) by the following procedure. About 0.5 g of catalyst was evacuated in a TPD cell at 623 K for 1.5 h. Ammonia as a probe base was adsorbed on the catalyst at 373 K for 0.75 h with the equilibrium pressure of 7.3 kPa and then evacuated at the same temperature for 0.75 h. TPD measurement of the sample was done from 373 K with a heating rate of 2.5 K min^{-1} and with helium as carrier gas having a flow rate of 60 cm^3 min^{-1}.

RESULTS

Reaction Conditions

The effect of reaction temperature on the side-chain alkylation of *p*-xylene with methanol on KX catalyst was examined at a temperature range of 653 to 723 K under a constant W/F and ratio of reactants. At 653 K, the side-chain alkylation did not proceed. As the reaction temperature in-

TABLE 2

Activity of Potassium Ion-Exchanged Zeolites

	SiO_2/Al_2O_3	Pore diameter (Å)	Yield (%)	
			MS	ET
KX	2.5	7.4	4.1	1.9
KY	5.0	7.4	Trace	0
KL	3.0	7.1	0	0
KM	9–10	6.7	0	0

creased up to 693 K, activity in the alkylation increased monotonicly and remained constant at 693 K, but at 723 K, the catalyst activity decreased rapidly with time-on-stream. The most suitable reaction temperature is 693 K in accordance with the side-chain alkylation of toluene with methanol (*3*, *9*). The other reaction conditions were the same as in the previous papers (*9*, *13*): W/F = 40 g · h/mol, carrier gas/F = 5.0 mol/mol, *p*-xylene/methanol = 6.0 mol/mol.

Activities of Potassium Ion-Exchanged Zeolites

Activities of various types of potassium ion-exchanged zeolites for the side-chain alkylation of *p*-xylene with methanol are shown in Table 2. The yields of *p*-methylstyrene(MS) and *p*-ethyltoluene(ET) were 4.1 and 1.9% on the KX catalyst. The KY catalyst gave only MS at a trace level. KL and KM have no activity for the side-chain alkylation. Thus, X type was more active than the other zeolites, in accordance with the side-chain alkylation of toluene (*9*).

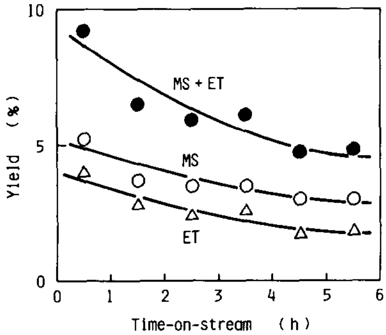

FIG. 1. Activity change with time-on-stream on RbLiX.

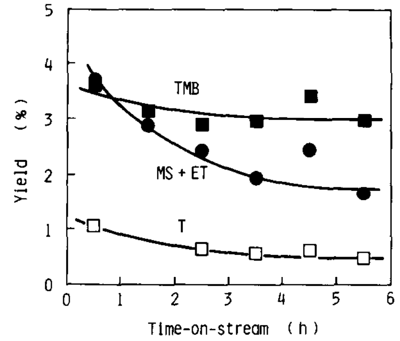

FIG. 2. Activity change with time-on-stream on KLiX.

Change in the Catalyst Activity

Figures 1, 2, and 3 show the changes in the activities of RbLiX, KLiX, and LiX with time-on-stream, respectively. On the RbLiX catalyst (Fig. 1), only MS and ET, products of the side-chain alkylation, were produced as aromatic products with a higher selectivity to MS. CO, H_2, and HCHO were also observed as light weight products. The yields of MS and ET decreased gradually with time-on-stream. This decrease may be due to continuous deactivation of the catalyst by coke deposition. RbLiX showed the highest activity for the side-chain alkylation of *p*-xylene with methanol in all the catalysts employed in the present paper. The results on KLiX catalyst were rather complicated as shown in Fig. 2. In addition to MS and ET, trimethyl-

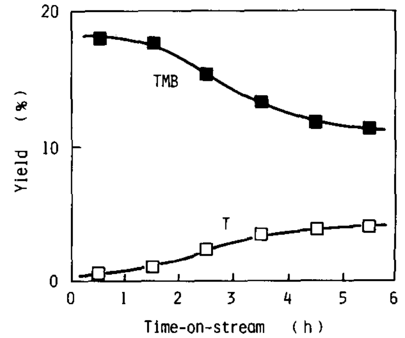

FIG. 3. Activity change with time-on-stream on LiX.

benzenes(TMB) and toluene(T) were also formed by the ring-alkylation, disproportionation, and/or demethylation of *p*-xylene. As to the light weight products, CH_4 and dimethyl ether were observed as well as CO, H_2, and HCHO. The yields of MS and ET decreased gradually, in the same way as those on RbLiX, while the yields of TMB and T decreased at first and then became almost constant. On the LiX catalyst (Fig. 3), only TMB and T were produced as aromatic products. With time-on-stream, the yield of TMB decreased but that of T increased gradually, and then both became almost constant. The yield of TMB on KLiX and LiX was much higher than that of T, indicating that the ring-alkylation of *p*-xylene with methanol was predominant compared to its disproportionation and demethylation.

Activity and Selectivity of Single-Ion-Exchanged Zeolites

Activities of single-ion-exchanged zeolites for the reaction of *p*-xylene and methanol are summarized in Table 3. In this reaction, catalysts are classified into two categories according to aromatic products. On LiX and NaX, TMB was produced predominantly as aromatic products, indicating that the main reaction was the benzene-ring alkylation of *p*-xylene with methanol. On K, Rb, and Cs exchanged X and Y zeolites, MS and ET were produced selectively without any other aromatic products, such as TMB and T. The side-chain alkylation forming MS and ET is catalyzed by the base catalysts (*2–6*), and the ring alkylation, disproportionation, and dealkylation, forming TMB and T, are catalyzed by the acid catalysts (*7, 8, 18, 19*). Thus, LiX and NaX have an acid nature, but K, Rb, and Cs ion-exchanged X and Y have a base nature. A similar result on the acid and base properties of alkali ion-exchanged X has been reported in the decomposition of 2-propanol to propene and/or acetone (*15*). The activity of X and Y type zeolites for the side-chain alkylation decreased in the sequence of KX > CsX > RbX, and CsY > RbY > KY, respectively. In the same alkali ion-exchanged X and Y zeolites, X types were more active than Y types. In the case of multivalent cation-exchanged zeolites,

TABLE 3

Activity of Single-Ion-Exchanged Zeolites for the Reaction of *p*-Xylene and Methanol[a]

	Yield (%)							
	Aromatics				Light weight products			
	MS	ET	TMB	T	FA	CO	DME	CH_4
LiX	0	0	18.1	0.6	0	0	3.2	3.0
NaX	0	0	6.3	0	0	4.6	4.8	2.4
KX	4.1	1.9	0	0	8.8	28.7	0	1.2
RbX	3.4	0.5	0	0	6.5	9.7	0	0.8
CsX	4.1	1.0	0	0	4.1	15.7	0	0
MgX	0	0	53.9	19.8	0	0	0.1	4.1
CaX	0	0	20.7	0.6	0	0	1.0	0.8
MnX	0	0	39.7	23.5	0	0	Trace	13.1
LaX	0	0	17.0	15.3	0	0	0.2	20.2
KY	tr	0	0	0	2.4	40.3	0	0.5
RbY	0.5	0	0	0	2.1	4.2	0	1.0
CsY	1.2	0	0	0	1.6	5.6	0	0

[a] MS, *p*-methylstyrene; ET, *p*-ethyltoluene; TMB, trimethylbenzenes; T, toluene; FA, formaldehyde; DME, dimethyl ether.

TMB and T were formed at a high yield. It is well known that these zeolites possess strong acid sites (*20*) and catalyze the ring alkylation, disproportionation, and dealkylation (*8*, *18*, *19*), resulting in the production of TMB and T. The fraction of 1,2,4-trimethylbenzene in TMB was more than 98% on all the catalysts having acid properties. Furthermore, isomerization of *p*-xylene was not observed on all the catalysts except for LaX on which a slight amount of *m*-xylene was produced.

The selectivity to light weight products also appears to depend on the acid and base properties of catalysts. Acid catalysts which are active for the formation of TMB and T yielded CH_4 and dimethyl ether, and base catalysts active for the side-chain alkylation yielded CO and HCHO. NaX showed exceptional behavior. NaX yielded only TMB as aromatic product, but it yielded CO as well as CH_4 and dimethyl ether. It should be noted that NaX is active for the side-chain alkylation of toluene with methanol (*3*). This will be discussed in detail later.

Activity of Two-Ion-Exchanged Zeolites

As mentioned above, the selectivity in the benzene-ring or side-chain alkylation is controlled by the cations present. The Li or Na incorporated X zeolite catalyzed the benzene-ring alkylation, and K, Rb, or Cs exchanged X catalyzed the side-chain alkylation. Thus, LiX and NaX act as acid catalysts, while KX, RbX, and CsX act as base catalysts. The base sites of alkali ion-exchanged zeolites are said to be $(AlO_4)^-$ paired with alkali ions (*15*). The basicity of $(AlO_4)^-$ would be induced by K, Rb, and Cs ions. In our recent note (*13*), it has been shown that the addition of Li cation to a base zeolite, RbX, accelerates the side-chain alkylation, as expected from the quantum chemical calculations, which suggests the importance of acid sites for the side-chain alkylation (*9*). It is of great concern how the activity and selectivity for the alkylation are affected by the two-ion exchange.

In Table 4, activities of two-ion-exchanged zeolites are summarized. Addition of Li to KX(KLiX) did not improve the performance of KX which was most active for the side-chain alkylation among the single-ion-exchanged zeolites. TMB and T as well as MS and ET were formed on KLiX. As to the light weight products, dimethyl ether was also formed. K and Li ions appear to work as base and acid sites, respectively. In the case of RbX, the effects of K, Li, Mg, and Ca ions were examined. In the case of K ion(RbKX), the total yield of MS and ET was not changed, although the selectivity to MS decreased. While, in the

TABLE 4

Activity of Two-Ion-Exchanged Zeolites for the Reaction of *p*-Xylene and Methanol[a]

	Yield (%)							
	Aromatics				Light weight products			
	MS	ET	TMB	T	FA	CO	DME	CH_4
KLiX	3.3	0.4	3.4	0.8	4.4	10.2	4.0	0.6
RbKX	2.3	1.2	0	0	2.5	15.8	0	0.1
RbLiX	5.2	4.0	0	0	1.6	17.2	0	0
RbMgX	1.0	0	1.0	1.2	1.2	3.1	12.4	0.4
RbCaX	0.1	1.4	1.7	0.8	0	3.4	4.8	Trace
CsKX	1.3	4.0	Trace	0	2.6	23.1	0.6	0.6
CsLiX	2.3	2.2	0.3	0	5.3	11.0	0	0.6

[a] MS, *p*-methylstyrene; ET, *p*-ethyltoluene; TMB, trimethylbenzenes; T, toluene; FA, formaldehyde; DME, dimethyl ether.

case of Li ion(RbLiX), the total yield of MS and ET was doubled compared to RbX. Both K and Li enhanced the formation of CO. When more acidic cations, such as Mg and Ca ions, were introduced into RbX, TMB, T, and dimethyl ether also were formed in a similar manner as on KLiX. These results indicate that the side-chain alkylation can be accelerated only by the suitable combination of acidic and base-inducing cations. Mg and Ca ions are too acidic for Rb, and the addition of them to RbX generate "strong" acid sites, resulting in the formation of TMB, T, and dimethyl ether. Although Li ion is too acidic for K, it gives an excellent combination with Rb for accelerating the side-chain alkylation. In the case of CsX with K ion(CsKX), total MS and ET were not affected but the selectivity to MS decreased similarly to RbKX. On CsLiX, a small amount of TMB other than MS and ET was produced. This TMB formation may be due to the higher degree of Li ion exchange, resulting in the generation of strong acid sites. Thus, the ratio of acid cation to base-inducing cation also appears to be an important factor.

Effect of the Ratio of Rb and Li Ions on the Activity

The effect of the ratio of acid cation to base-inducing cation was examined in the case of RbLiX. The results are summarized in Table 5. The catalysts were prepared by simultaneous ion exchange of 13X with an aqueous solution of a mixture of RbCl and LiCl with a molar ratio of x(Rb/Li). On the RbLiX catalysts with more than 0.15 of the Li/Rb+Li ratio, TMB was formed as well as MS and ET, but T was not observed. On RbLiX (*4*), only MS and ET were formed at higher yields, and the selectivity to MS was higher than RbLiX as shown in Table 4. In the light products, CO and HCHO were formed, but CH_4 and dimethyl ether were not detected on all RbLiX catalysts. Figure 4 shows the change in the yields with the ratio of Rb and Li ions of RbLiX including both two-stage-ion-exchanged and simultaneously ion-exchanged RbLiX. The activity for the side-chain alkylation was remarkably increased by the introduction of a small amount of Li ions to RbX. However, further increase in Li content reduced the activity for the side-chain alkylation and generated active sites for the benzene-ring alkylation similarly to the case of CsLiX.

Relationship between the Total Yield of MS and ET and the Yield of CO

By-products in the present reaction are TMB, T, dimethyl ether, CH_4, HCHO, and

TABLE 5

Effect of the Degree of Lithium Ion Incorporation into RbX[a]

	$\frac{Li^b}{Rb + Li}$	Yield (%)							
		Aromatics				Light weight products			
		MS	ET	TMB	T	FA	CO	DME	CH_4
RbX	0	3.4	0.5	0	0	6.5	9.7	0	0.8
RbLiX (4)	0.15	5.3	2.7	0	0	1.8	19.1	0	0
RbLiX (3)	0.21	2.0	0	0.1	0	5.2	6.5	0	0
RbLiX (2)	0.23	1.8	0	0.2	0	6.0	5.0	0	0
RbLiX (1)	0.37	2.0	0	0.1	0	1.3	6.4	0	0
LiX	1.0	0	0	18.1	0.6	0	0	3.2	3.0

[a] MS, *p*-methylstyrene; ET, *p*-ethyltoluene; TMB, trimethylbenzenes; T, toluene; FA, formaldehyde; DME, dimethyl ether.

[b] Atomic ratio of Li to Rb + Li ion-incorporated in zeolites.

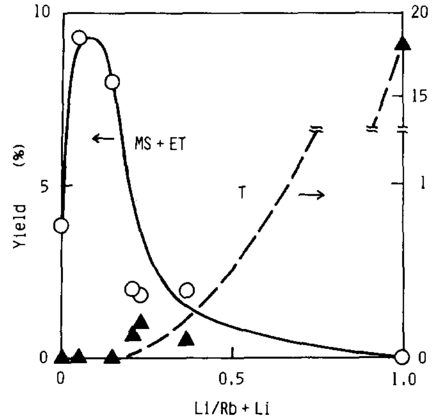

FIG. 4. Effect of Li ion content in a series of Rb and Li ion-exchanged X.

CO. TMB, T, dimethyl ether, and CH_4 are formed on acid catalysts, and the formation of these by-products can be minimized by using base catalysts which are active for the present reaction. However, the formation of MS and ET is always accompanied by the formation of HCHO and CO. HCHO is an alkylating reagent for the side-chain alkylation, but CO is an undesirable product. According to the reaction mechanism reported previously (*2*, *3*, *9*), MS and ET are formed as main products by the reaction of *p*-xylene and HCHO which is formed by the dehydrogenation of methanol, and further decomposition of HCHO leads to the formation of CO. The ratio of the yield of CO(Y_{CO}) and the total yield of MS and ET(Y_{MS+ET}) indicates the selectivity of the reaction of HCHO to further decomposition or the side-chain alkylation. The relationship between Y_{MS+ET} and Y_{CO} is shown in Fig. 5. Catalysts containing all the single- and two-ion-exchanged zeolites were classified into three groups: first, KX, CsKX, and RbKX containing K ion as a secondary cation; second, CsX, RbX, and NaX containing Na ion; and third, a series of RbLiX, CsLiX, KLiX, and LiX containing Li ion. In the first group, Y_{CO} increased more steeply with increasing Y_{MS+ET} than in the other two groups, indicating that the ratio of the decomposition to the side-chain alkylation in the first group is larger than that in the other two groups. The third group containing Li ion shows the lowest Y_{CO} at the same Y_{MS+ET}. In other words, a small amount of Li ion incorporation to other cation-exchanged zeolites prevents the decomposition of HCHO which is an alkylating reagent. As discussed in the following section, enhancement of basicity accelerates the dehydrogenation of methanol to HCHO, but too strong basicity is accompanied by further decomposition of HCHO. The addition of Li may control the basicity of the catalyst to produce HCHO from methanol without decomposing it.

DISCUSSION

Comparison of Toluene and p-Xylene as a Reactant

Several similar points have been observed in the side-chain alkylation of *p*-xylene and toluene. In both reactions, the optimum reaction temperature is 693 K and X type zeolites are more active than the Y varieties for the side-chain alkylation (Table 3). Furthermore, formaldehyde is detected, indicating that *p*-xylene reacts with methanol through the same reaction pathway as toluene. But a big difference is observed on NaX. It has been reported that on the NaX catalyst toluene converted into styrene and ethylbenzene by the side-chain alkylation with methanol (*3*). On the other hand, as can be seen from Table 3, *p*-xylene converted into trimethylbenzenes(1,2,4-TMB > 98%) by the benzene-ring alkylation on the same catalyst, NaX. Thus, NaX

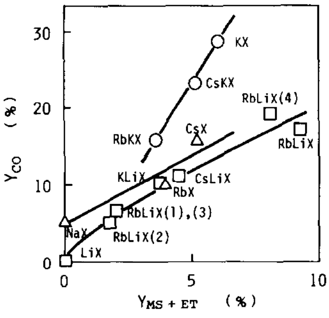

FIG. 5. Relationship between the total yield of MS and ET and the yield of CO.

acts as a base catalyst for the alkylation of toluene and as an acid catalyst for *p*-xylene. The distribution in light weight products shown in Table 3 also indicates that NaX has both acid and base properties. Both CO and dimethyl ether were formed on NaX, though, on other single-ion-exchanged zeolites, either CO or dimethyl ether was formed: CO and HCHO were formed on base catalysts and dimethyl ether was formed on acid catalysts. These facts suggest that methanol is converted into both intermediates for the side-chain and the benzene-ring alkylation. Thus, the selectivity to the side-chain alkylation or to the benzene-ring alkylation on NaX should be attributed to the nature of aromatic molecules. Since the methyl group has the electron-donor character to the benzene ring, resulting in the enhancement of its basicity, the benzene ring of *p*-xylene is more basic than that of toluene. Therefore, it is concluded that the selectivity of NaX for the alkylation is determined by the comparison of the intrinsic acid–base property of NaX and the basicity of aromatics: in other words, the side-chain alkylation proceeds in the case of a relatively acidic aromatic compound, and the ring alkylation proceeds in the case of a relatively basic one.

Activities of Single- and Two-Ion-Exchanged Zeolites for the Alkylation of p-Xylene

In the case of single-ion-exchanged zeolites, multivalent cation, Li and Na ion-exchanged zeolites produced TMB and T as acid catalysts, while K, Rb, and Cs ion-exchanged zeolites produced MS and ET as base catalysts. As reported previously (*13*), the addition of Li ion into RbX accelerates the side-chain alkylation, supporting the results of quantum chemical calculations (*9*). As can be seen from Table 5 and Fig. 4, the activity for the side-chain alkylation is maximum with the addition of a small amount of Li ions. This result indicates that this alkylation is sensitive to the nature of acid sites. Thus, the alkylation is affected by the subtle change of the acid–base property of catalysts. In order to consider comprehensively the activities of all catalysts for the reaction of *p*-xylene and methanol, a common measure of the acid–base properties of various zeolites is necessary.

It has been reported that the activities of many reactions, such as cracking and isomerizations, on the zeolites ion-exchanged with more than one cation other than proton are related to the electrostatic field and electrostatic potential (*14, 21*) and also to the amount of acid and its strength (*22*). Also, good correlations of the electrostatic field, electrostatic potential, and the amount and strength of acid have been observed (*21*). In the present study, the electrostatic potential (e/r) of the cation present is used as a tentative measure of the acid–base property of catalyst. As the zeolites employed contain metal cations, the arithmetic means of electrostatic potentials of cations is calculated according to the following equation in order to show the overall acid–base property of the zeolite for convenience:

$$\text{Electrostatic potential } (e/r) = \sum_i e_i/r_i \times f_i,$$

where e_i, r_i, and f_i stand for the charge, ionic radius, and degree of ion exchange of the i cation, respectively. It is considered that a larger value of e/r means that the catalyst becomes more acidic. In Fig. 6, the total yield of MS, ET, CO, and HCHO, the yield of dimethyl ether(Y_{DME}), and the yield of TMB minus T(Y_{TMB-T}) are plotted against e/r over all the single- and two-ion-exchanged zeolites. The total yield of MS, ET, HCHO, and CO stands for the overall dehydrogenation of methanol to HCHO with the further conversion of HCHO taken into consideration. Y_{TMB-T} can be a measure of the conversion of methanol in the benzene-ring alkylation. TMB is formed by both the ring alkylation and disproportionation, while T is formed by the disproportionation and demethylation. On most of the catalysts, the yield of CH_4 is not so

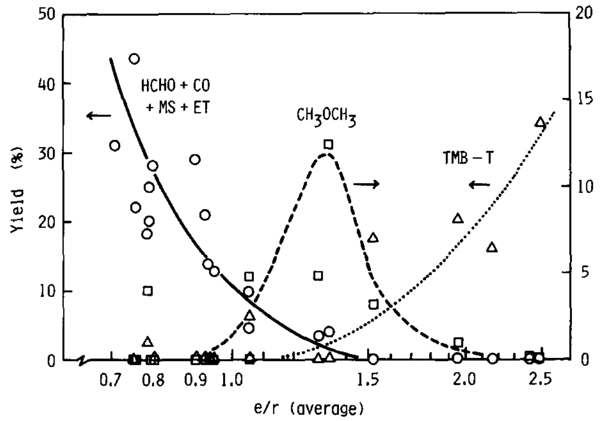

FIG. 6. Change in yields of products related to methanol.

large that demethylation can be ignored. Y_{TMB-T} on MnX and LaX are omitted because of the large yield of CH_4. As shown in Fig. 6, methanol is active in the benzene-ring alkylation at large values of *e*/*r*, and methanol converts to dimethyl ether by the dehydration at a medium value of *e*/*r*. These results indicate that the benzene-ring alkylation requires stronger acid sites compared to the dehydration of methanol. At small valves of *e*/*r*, methanol is dehydrogenated to formaldehyde, some of which is consumed in the side-chain alkylation and also in the decomposition to CO and H_2. These reactions may proceed under the effect of base sites, because the catalyst at small values of *e*/*r* exhibits the base property (*3*) and catalyzes the dehydrogenation of 2-propanol (*15*).

In Fig. 7, the total yield MS and ET (Y_{MS+ET}) produced by the side-chain alkylation, and the yields of TMB(Y_{TMB}) and T(Y_T) are plotted against the value of *e*/*r*. Y_{TMB} and Y_T increased gradually with the increase of *e*/*r*, indicating that the benzene-ring alkylation and disproportionation proceed on the acid catalyst and are accelerated on the stronger acid in accordance with the results reported previously (*6*, *8*, *23*). On the other hand, the activity for the side-chain alkylation increased steeply as the value of *e*/*r* decreased. This

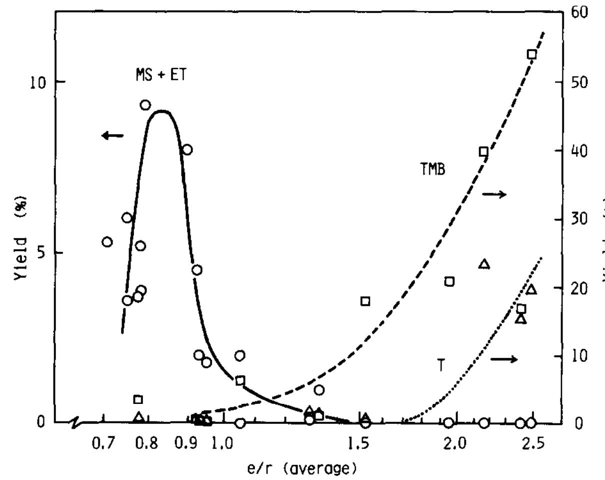

FIG. 7. Change in yields of products related to *p*-xylene.

result indicates that the side-chain alkylation proceeds on the base catalyst in accordance with the results reported by Yashima *et al.* (*3*) and Sodesawa *et al.* (*6*). However, as *e*/*r* decreased further, Y_{MS+ET} passes the maximum value, followed by the rapid decrease of Y_{MS+ET}. According to quantum chemical calculations (*9*), in the side-chain alkylation of alkylbenzenes formaldehyde attacks the methyl group of alkylbenzenes to form the vinyl group. In this pathway, the formation of formaldehyde and the activation of methyl group are essential. As mentioned above, the base sites are important in the formation of formaldehyde. This may result in the increase of Y_{MS+ET} as *e*/*r* decreased from 1.5 to 0.9 in Fig. 7. The existence of the maximum value of Y_{MS+ET} at a suitable *e*/*r* indicates that the activation of alkylbenzene requires acid sites. The results on NaX indicate that base sites are also necessary. As mentioned above, the side-chain alkylation of *p*-xylene does not proceed, although the alkylating reagent, HCHO, is formed and the side-chain alkylation of toluene proceeds on NaX. Thus, both acid and base sites are necessary for the activation of alkylbenzene, as predicted by quantum chemical calculations (*9*). These also suggest that the activation of alkylbenzene is more important for the side-chain alkylation than the formation of HCHO, because at both sides of the maximum in Fig. 7, KX(*e*/*r* = 0.75) and NaX(*e*/*r* = 1.05), the yields of MS and ET were not so large in comparison with the relatively large total yield of HCHO, CO, MS, and ET.

Active Sites of Two-Ion-Exchanged Zeolites

In the previous section, the importance of acid sites in the side-chain alkylation is shown in the plot of yield against *e*/*r*. The acid property of the two-ion-exchanged zeolites was examined by using Hammett indicators to measure $H_{0\,\max}$ and by using the temperature-programmed desorption(TPD) of ammonia. In the latter, the acid amount was determined from the desorbed amount of ammonia and the acid strength from the temperature of the peak maximum (T_M). In Table 6, the acid properties of some catalysts (mainly active catalysts for the side-chain alkylation) are summarized together with Y_{MS+ET} and the value of *e*/*r*.

$H_{0\,\max}$ of RbKX and RbX are +4.0 and those of RbLiX(4) and RbLiX(1) are +3.3. The latter is identical to that of LiX. The peak maximum temperatures (T_M) of the catalysts containing Li ions are essentially identical to T_M of LiX. These results indicate that the introduction of Li ions to the RbX catalyst results in the enhancement of the acid strength. However, the increase in the acid amounts by the introduction of Li ions is very little compared with the acid amount of LiX. Therefore, the introduction of a small amount of Li ions has much more effect on the strength of acid sites than on the amount. RbLiX(4) which shows higher activity for the side-chain alkylation has stronger acid sites than RbX, supporting the prediction by quantum chemical calculations (*9*) that the cooperation of acid and base sites is very important in the side-chain alkylation.

In the preceding sections, the active sites for alkylation have been discussed on the basis of acid strength, such as *e*/*r*, $H_{0\,\max}$, and T_M. It is considered from the standpoint of the atomic scale that, in alkali ion-ex-

TABLE 6

Y_{MS+ET}, TPD method, H_0 max, and *e*/*r*[a]

	Y_{MS+ET} (%)	T_M (K)	Amount (mmol/g)	$H_{0\,\max}$	*e*/*r* (average)
RbKX	3.5	427	0.10	+4.0	0.75
RbX	3.9	427	0.10	+4.0	0.79
RbLiX	8.0	466	0.25	+3.3	0.90
RbLiX (1)	2.0	468	0.18	+3.3	1.05
RbMgX	1.0	440 551	0.32	—	1.33
LiX	0	460	1.50	+3.3	1.52

[a] $e/r = \sum_i e_i/r_i \times f_i$, where e_i, r_i, and f_i represent charge, ionic radius, and degree of ion exchange of *i* cation, respectively.

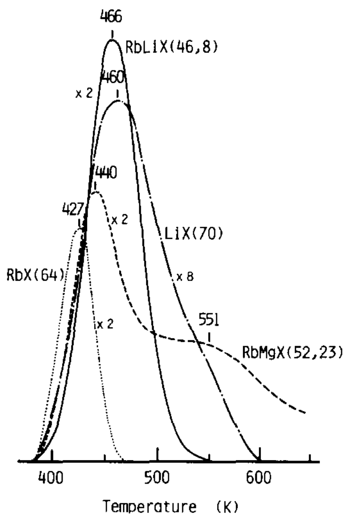

FIG. 8. TPD spectra of ammonia on various zeolites.

changed zeolites, weak acid sites may be formed by cations and base sites may be the oxygen atoms in the lattice $(AlO_4)^-$ paired with the alkali cations. In Fig. 8, TPD spectra of ammonia on RbX, RbLiX(4), LiX, and RbMgX are shown. TPD spectra other than RbMgX have only one peak. However, the TPD spectrum on RbMgX has two peaks called low and high peaks. The T_M of the low peak of RbMgX is near the T_M of RbX and that of the high peak is higher than that of LiX, indicating that the acid strength of this peak is stronger. This result suggests that low and high peaks are related to Rb and Mg ions, respectively, or, in other words, Rb and Mg ions form adsorption sites for ammonia independently of each other. These ions appear to work as different catalytic sites, because both the side-chain and the benzene-ring alkylations proceeded on RbMgX as shown in Table 4. Rb and Mg ions may work as active sites for the side-chain alkylation and ring alkylation, respectively, as expected from the results on RbX and MgX shown in Table 3. However, there should be some interaction between Rb and Mg ions. The yields of MS+ET and TMB+T on RbMgX are much less than the yield of MS+ET on RbX and that of TMB+T on MgX. On NaX, either the side-chain or benzene-ring alkylation proceeds depending on the kind of aromatic reactants. However, when NaX contains very small amounts of multivalent cations as impurity, both alkylations of toluene proceeds (*3*). KLiX and RbCaX also catalyzed simultaneously both alkylations of *p*-xylene producing a mixture of MS, ET, TMB, and T. These observations also support the above conclusion that the two kinds of cations play different roles. In the case of a series of RbLiX, only one peak could be observed in TPD spectra. However, this peak may result from an overlap of two peaks due to Rb and Li ions, because the maximum temperatures on RbX and LiX are so close to each other. The independent role of two ions in RbLiX is suggested by the result that both the side-chain and benzene-ring alkylation proceeded on RbLiX containing more than 0.2 of the Li/Rb + Li ratio. Again there should be some interaction between Rb and Li, because the yields of MS+ET and TMB on these catalysts were less than that of MS+ET on RbX and that of TMB on LiX, respectively. TPD spectra shown in Fig. 8 also show the interaction. The desorption peak from LiX had a tailing up to a temperature higher than that from RbLiX. This result indicates that the stronger acid sites on LiX are weakened by the coexistence of Rb ions. If the Li content is small, the acid strength of Li ions is weakened sufficiently by Rb ions to prevent the ring alkylation. With increasing Li content, the effect of Rb ions on the acid strength of each Li ion would decrease, resulting in the ring alkylation. But the acid strength of Li ions is not as strong as that in LiX, which results in a low yield of TMB. Based on quantum chemical calculation the roles of acid and base sites in the side-chain alkylation of toluene are summarized as follows (*9*). The base site makes the carbon atom of the side chain more active than that of the benzene ring. The role of acid sites is attributed to the adsorption and stabilization of toluene. In RbLiX, the acid site to adsorb and stabilize alkylbenzene is the Li ion whose acid strength is weakened by the effect of Rb ion. The base site to activate the carbon atom in the alkyl group is the oxygen atom in the lattice $(AlO_4)^-$ whose basic property is enhanced by Rb ion but may be reduced by Li ion. On KLiX, significant ring alkylation proceeded in spite of very small Li content. The base-inducing power of K ions is not strong enough to weaken the acid strength of Li ions. Thus, the optimum combination and contents of acid cation and base-inducing cations depend on the acidic and base-inducing properties of cations. The optimum combination and contents would depend on the basicity of alkylbenzene, too. As mentioned above, NaX acts as an acid catalyst for *p*-xylene and as a base catalyst for toluene. The effect of cation positions must be considered.

CONCLUSION

On the basis of the experimental results, the side-chain alkylation proceeds generally on the base catalysts. However, as shown in Fig. 7, an optimum strength of acid sites exists and the optimum catalysts, such as RbLiX and RbLiX(4), have slightly stronger acid sites as shown in Table 6 and Fig. 8. Moreover, the catalysts with much stronger acid sites catalyze the benzene-ring alkylation. Therefore, it has been proved experimentally that weak acid sites as well as base sites are important for the side-chain alkylation, as predicted by quantum chemical calculations (*9*). It is also shown that the introduction of a small amount of Li ions to base zeolites prevents the decomposition of formaldehyde formed from methanol (Fig. 5), resulting in the higher selectivity to MS than ET.

In the case of two-ion-exchanged zeolites, it is shown that each cation can separately form an active site under their mutual effect. The optimum composition of these two active sites comprising the active center could result in the highest activity for the side-chain alkylation.

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