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O-alkylation of phenol derivatives over basic zeolites

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Abstract

Alkali metal loaded zeolite X was used to catalyze O-alkylation of phenol derivatives in the presence of excess methanol. The reactivity of zeolite in the O-alkylation increased as the basicity of ion-exchanged metals increased. The super base originated from cesium oxide particles in zeolite cavities was as equally active as the ion-exchanged cesium cation. Hence the reactivity of the Cs loaded zeolite was found to be proportional to the total amount of cesium in zeolites. In addition to mono and dialkylphenols, the phenol derivatives with hydroxy, amino, nitro and chloride group were also used as reactants to investigate the effect of acidity of reactants on the reaction. The conversion increased as the acidity of hydroxy group of reactant increased. But the strong acidity resulted in rapid deactivation of the catalyst. Except for aminophenol the reaction products were the corresponding O-alkylated products regardless of functional groups attached and for aminophenol, N-alkylated product was produced due to the strong acidity of the amino group. The high selectivity to O-alkylation reaction over base catalyst was not a function of the conversion and thought to have resulted from the suppression of the side reactions such as C-alkylation of phenol and anisole which occurred predominantly on the acidic sites. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: O-alkylation; Phenol; Basic zeolite

1. Introduction

There has been growing interest in the use of zeolites for the solid acid or solid base catalysts [1–4]. Acidic zeolites have been used widely in a number of important reactions. In contrast, only a few reactions and characterization methods for the basic zeolites have been known to date [5]. O-alkylation of phenol with methanol is one of them investigated recently by Kim and co-workers [6]. In their paper, the reaction, conventionally proceeded in the liquid phase using the bases such as NaOH and K_2CO_3 in the presence of dimethyl sulfate (DMSA), was catalyzed by solid base zeolites. Methanol was used instead of DMSA to supply the methyl group, and 100% selectivity was maintained even to very high conversion of phenol. Many authors using the acidic catalysts reported that high selectivity to anisole in O-alkylation of phenol with alcohol was found in low conversion and the main reactions were ring alkylations to produce cresol or xylenol [7–9]. Using dimethylcarbonate as a methylating agent, Ono et al. [10] reported that 92% anisole yield was attained over NaX.

In this study, O-alkylation of various phenol derivatives with methanol over basic zeolites was carried out in the gas or slurry phase to investigate the effects of basicity of the catalyst and functional group of benzene ring on the reaction.

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2. Experimental

2.1. Preparation of catalysts

Cs loaded zeolite X samples with various Cs loadings were prepared by the conventional ion-exchange method with cesium acetate solution. Rinsing method, in which ion-exchanged zeolites were filtered and dried without further washing, was also used to introduce Cs-oxide particles into the zeolite cavities [11,12]. All the catalysts were calcined under air at 500°C for 4 h. The loadings of Cs were analyzed by atomic absorption (AA) and the presence of cesium oxide particles was confirmed by thermal gravimetric analyzer (TGA).

2.2. O-alkylation reaction

The catalysts were tested in the vapor or liquid phase. The vapor phase reaction was carried out in a fixed bed reactor (25 cm long and $\frac{1}{4}$ in. SS tube) containing 0.05 g of catalyst at 1 atm and in the temperature range between 250°C and 290°C. The reactants, phenol derivatives and methanol, were introduced to the reactor by using saturators and nitrogen stream. The mole ratio of the phenol to methanol was 1:8 and it was adjusted by controlling the temperature of each saturator. The total flow rate of the reactant mixture was 20 ml/min and feeding rate of the phenol derivatives was 3.0×10^{-6} mol/min. The product mixture was analyzed by gas chromatography (GC). For the slurry phase reaction, an autoclave reactor with 300°C internal volume was used. After the reaction of phenol derivatives and excess methanol for 2 h in the temperature range from 200°C to 260°C, the product was separated from solid catalyst and analyzed by GC.

3. Results and discussion

3.1. The effect of basicity of catalyst on the O-alkylation of phenol

The basicity of the zeolite catalyst is dependent on the types of cation ion-exchanged and the preparation method [13]. Fig. 1 shows the catalytic activities of Na zeolites ion-exchanged with various alkali metals after reaction for 1 h. As the basicity of the metal increased from Na to Cs, the conversion increased. The conversion level was well correlated with the ionization potential of the alkali metal used. The product from the reaction was only anisole for all the base catalysts used.

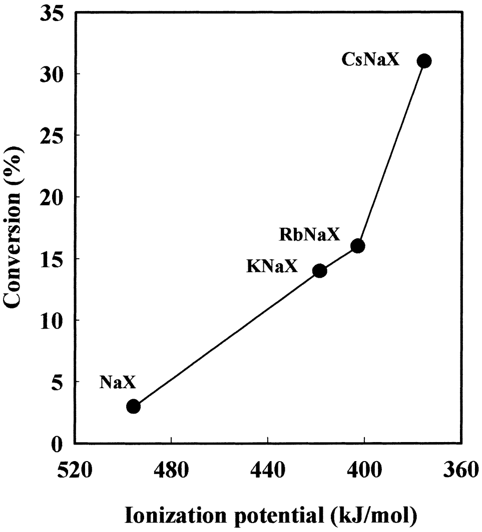

Fig. 1. Catalytic activities of zeolites ion-exchanged with various alkali metals as a function of ionization potential of alkali metals.

It was reported by several authors [11–13] that depending on the preparation methods the basicity of Cs loaded zeolite was much varied. Notably the cesium oxide particles in zeolite cavity, prepared by the rinsing method in which zeolite was only filtered without subsequent washing after ion-exchange step, has been known to exhibit the super basicity [11–13]. Thus prepared super base was known to catalyze such reactions as isomerization of 1-butene to *cis*-2-butene and dehydrogenation of isopropyl alcohol to acetone, whereas the ion-exchanged Cs cations showed very low activity in those reactions.

For Cs ion-exchanged zeolites, the extent of Cs cation was varied from 7% to 50% depending on the concentration of Cs acetate solution used in the ion-exchange step. We denote the ion-exchanged zeolites and rinsed zeolite as CsNaX-*n*I and CsNaX-*n*I-*m*R, respectively, where *n* is the concentration of the Cs acetate solution used in the ion-exchange step and *m* is the acetate concentration used in the rinsing step. The rinsed zeolites contained the occluded Cs acetate in the samples in addition to the exchanged Cs cation.

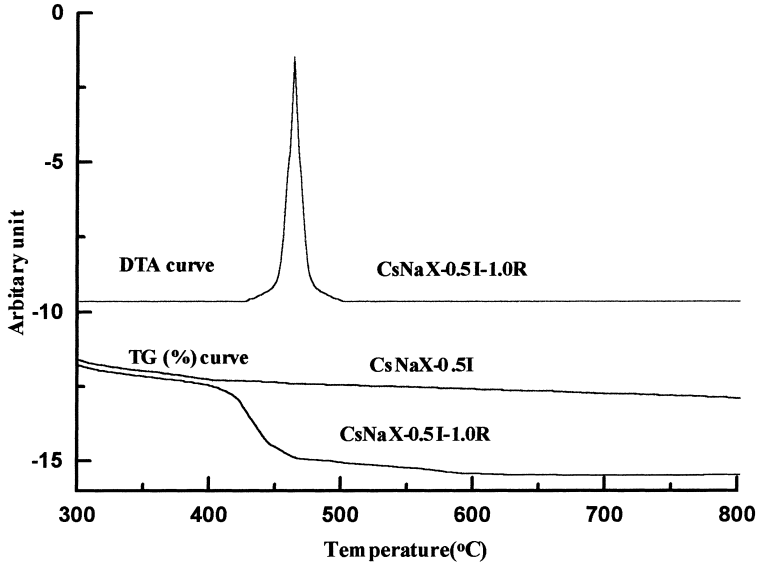

Fig. 2. Thermal gravimetric analysis of Cs ion-exchanged zeolites and Cs rinsed zeolites.

The presence of occluded Cs acetate was confirmed by the decomposition peak of Cs acetate at 430°C in TGA [6,11,12] as shown in Fig. 2. Thus for rinsed zeolite Cs oxide particles with strong basicity were formed from the occluded Cs acetate in the zeolite cavities. The number of Cs atoms per unit cell estimated by TGA and AA was in the range from 4 to 12, as shown in Table 1.

Fig. 3 shows the catalytic activities of Cs ion-exchanged zeolites (CsNaX-*n*I) and Cs rinsed zeolites (CsNaX-*n*R) in *O*-alkylation of phenol with methanol as a function of Cs loading. In both cases, the catalytic activity showed a maximum with increasing amount of Cs loading. It can also be seen in the figure that the catalytic activities are dependent upon the total amount of Cs loaded either ion-exchanged or occluded. The big difference in catalytic activity between cesium cation and cesium oxide reported by many authors [11,12] was not found in this reaction, indicating that ion-exchanged cesium cations also have enough basicity to alkylate the hydroxy group of phenol. The decrease in the activity after

Table 1
Occluded Cs per zeolite unit cell

Catalysts	Cs (wt%)	No. of Cs per unit cell by AA	No. of Cs per unit cell by TGA
CsNaX-0.5I	22[a]	–	–
CsNaX-0.5I-0.2R	24	4.1	3.5
CsNaX-0.5I-0.5R	26	8.4	7.4
CsNaX-0.5I-1.0R	28	12.9	12

[a] Percentage of ion-exchanged Na by Cs is 42%.

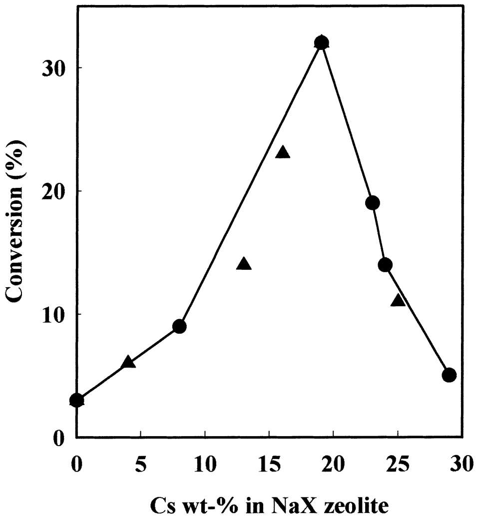

Fig. 3. Catalystic activities of various CsNaX zeolites in *O*-alkylation of phenol as a function of cesium loading. (●) Rinsed zeolites and (▲) ion-exchanged zeolites.

Table 2
Surface area of cesium loaded zeolites

Catalysts	Surface area (m^2/g-cat.)
NaX	588
CsNaX-0.5I	375
CsNaX-0.5I-0.2R	350
CsNaX-0.5I-0.5R	320
CsNaX-0.5I-1.0R	277

the maximum was interpreted to be due to the diffusional limitation of reactants and/or products [6]. This may be deduced from the observation that the BET surface areas of both catalysts decreased rapidly with the loading as shown in Table 2.

3.2. *The effect of acidity of reactant*

The catalytic activities of Cs ion-exchanged zeolite (CsNaX-0.5I, 42% ion exchanged) in *O*-alkylation of phenol, mono and dimethylphenol with methanol is shown in Fig. 4 as a function of reaction time. The selectivity to the methoxybenzene compounds, i.e., anisole compounds, was 100% in all the experiments. Among the reactants, phenol showed the highest initial activity. The initial activity decreased as the number of methyl group in the reactant increased. Although there is a rapid deactivation for phenol, the higher initial activity can be ascribed to the stronger acidity of phenol than that of mono or dimethylphenol, since the acidity is weakened by the presence of alkyl groups in the benzene ring. In a separate experiment, it was also found that the mole ratio of methanol to phenol lower than 4 caused a rapid deactivation of the catalysts.

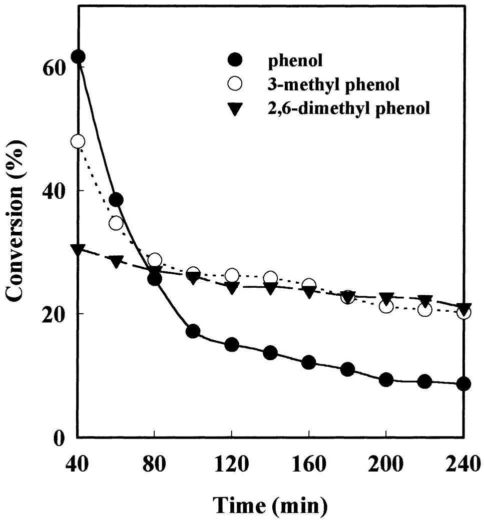

Fig. 4. Catalytic activities of Cs ion-exchanged zeolite in *O*-alkylation of phenol derivatives with methanol. (Mole ratio of phenol deriviatives to methanol=1/8.3; reaction temperature: 270°C.)

The phenol derivatives with different acidity and functional groups such as nitro, chloro, amino, and hydroxy group were used to test the effects of these functional groups on the catalytic activity of *O*-alkylation. Among the functional groups, methyl, hydroxy, and amino group are electron donating groups and hence lower the acidity of the corresponding reactants, while chloro and nitro groups are electron withdrawing groups and increase the acidity. Because of the high boiling points of the reactants, the reaction was carried out in the liquid phase with excess methanol.

Table 3 shows the results of the slurry phase *O*-alkylation using CsNaX-0.5I catalysts at 230°C for 2 h. Depending on the acidities of the reactants, different product distributions were obtained. The nitrophenol (pK_a=7.2) showed the highest conversion among the reactants used. This could be explained by the strong acidity of nitrophenol (pK_a=7.2) when compared with that of phenol (pK_a=10). For aminophenol, however, mono- or di-*N*-alkylated products were mainly produced rather than *O*-alkylated product, because of the stronger acidity of the aryl amino groups (pK_a value of the conjugate acid, anilinium ion=4.6) than that of the hydroxy group (pK_a=10).

Hydroquinone was also tested in liquid phase and the results are shown in Table 4. 4-Methoxyphenol, which is a valuable intermediate for perfume and flavor industries and especially food additives like vanilline, is produced from *O*-alkylation of hydroquinone by using a Cs ion-exchanged base zeolite used in this study. To produce the monomethoxyphenol selectively, Williamson ether synthesis and many solid acid catalysts have been tried [14,15]. But it was very difficult to increase the selectivity because of the byproducts produced from *C*-alkylation. By using the Cs ion-exchanged zeolite, 4-methoxyphenol was selectively produced in the temperature range from 220°C to 240°C as shown in Table 4. Above 290°C, the fraction of dimethoxybenzene increased rapidly

Table 3
The reactivites of CsNaX zeolites in the slurry phase *O*-alkylation at 230°C

Reactant	Conversion (%)	Selectivity (%)		
		O-alkylation	*C*-alkylation	*N*-alkylation
4-Nitrophenol	48.5	96	4	–
4-Aminophenol	4.8	–	–	100
4-Chlorophenol	2.2	42.8	57.6	–
Phenol	2.6	100	–	–

Table 4
The activities of CsNaX-05I in alkylation of hydroquinone at various temperatures

Catalyst	Reaction temperature (°C)	Conversion (%)	Selectivity (%)		
			Monomethoxyphenol	Dimethoxybenzene	Etc.
CsNaX-0.5I	220	11.1	100	–	–
	240[a]	19.7	100	–	–
	240	43.0	95	5	0
	260	76.0	88	11	1
	290	97.9	70	28	1
	220[b]	27.4	94	2	4
	290[b]	98.0	56	33	11

[a] Reaction time 0.5 h.
[b] Reaction time 6 h.

with conversion, indicating that the monomethoxyphenol produced further reacted with methanol to make dimethoxybenzene. In a separate experiment, the conversion of Cs ion-exchanged zeolite in the reaction was five times higher than that of NaX or NaY.

3.3. The effects of basic and acidic sites

It was reported that solid acid catalysts could be used to catalyze alkylation of phenol with methanol [7–9]. With acid catalysts, however, *C*-alkylated products such as cresol and xylenol are also produced simultaneously in addition to *O*-alkylated product, i.e., anisole. Especially, *C*-alkyated products are the main products at high conversion, indicating that the selectivity is a function of conversion for the acid catalyst. To estimate the dependency of selectivity on the conversion of the base catalyst, the conversion of the alkylation reaction using Cs ion-exchanged basic zeolite (CsNaX-0.5I, 42% ion exchanged) was increased as shown in Fig. 5. As the amount of catalyst increased, conversion was increased up to 100%. But there was no variation in selectivity, i.e., only anisole was produced in all the cases. This means that the selectivity to anisole is no more a function of conversion. To compare the catalytic role of base

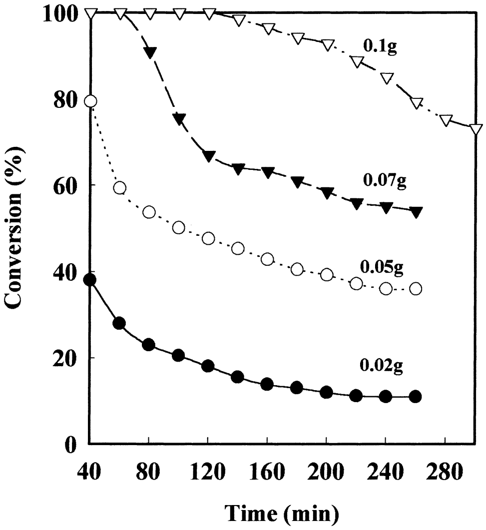

Fig. 5. The relationship between conversion and the catalyst loading with time. (Mole ratio of phenol to methanol=1/8.3; reaction temperature: 290°C.)

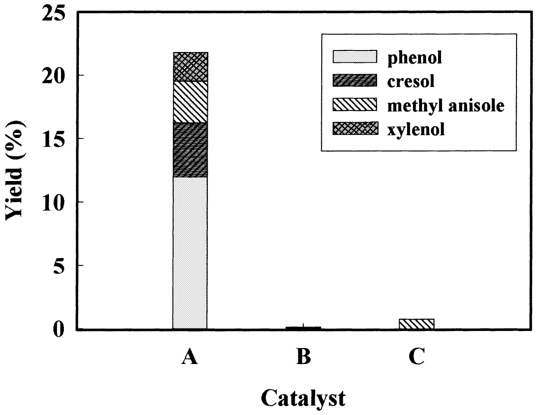

Fig. 6. Product distribution from the reaction of anisole alone over acid and base catalysts. A: Al_2O_3, B and C: CsNaX-0.5I. Reaction temperature: A and B: 270°C; C: 300°C.

catalyst and that of acid catalyst, only anisole was used as a reactant in the absence of methanol. The products from the reaction are compared in Fig. 6. With acidic catalyst (alumina), phenol, cresol, methylanisole and xylenol were produced at 270°C, whereas no significant products were obtained with base catalyst (CsNaX-0.5I). Even at 300°C, the conversion of the reaction was less than 2% with base catalyst and only trace amount of methylanisole was produced. These results suggested the various reaction pathways for the acid catalyst such as decomposition of anisole to phenol and direct ring-alkylation to cresol, methylanisole and xylenol, resulted in the poor selectivity in the alkylation of phenol. Thus it can be concluded that the high selectivity to anisole from a base catalyst is due to suppression of such side reactions occurring in the acid catalysts.

4. Conclusions

O-alkylation of phenol was catalyzed by the alkali metal-loaded zeolites. The reactivity of the catalyst increased with basicity of the loaded metal and there was no difference in catalytic activity between Cs cations ion-exchanged and Cs oxide particles in zeolite cavity. The high selectivity to anisole over basic Cs ion-exchanged zeolite is no more a function of conversion.

The acidity of reactant affected significantly the initial reaction rate and product distribution in a base catalyzed reaction. So far, the nitrophenol, which is the strongest acidic reactant among the reactants used, shows the highest reactivity. In case of aminophenol, *N*-alkylated products rather than *O*-alkylated ones were mainly produced due to the stronger acidity of amino group than that of hydroxy group. Also methoxyphenol, which is a valuable intermediate for perfume and flavor industries and especially food additives like vanilline, is selectively produced from *O*-alkylation of hydroquinone by using a Cs ion-exchanged base zeolite.

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