

Selective *O*-Alkylation Reaction of Hydroquinone with Methanol over Cs Ion-Exchanged Zeolites

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Abstract—*O*-alkylation reaction of hydroquinone with excess methanol was performed by using alkali metal ion-exchanged zeolite catalysts in a slurry type reactor to substitute the solid zeolite catalysts for the homogeneous liquid phase catalysts. This was also done to produce selectively mono-alkylated 4-methoxyphenol, a valuable intermediate for the perfume, flavor, food and photo industries. The effects of the basicity of various zeolites and reaction conditions such as temperature, reaction time and the amount of catalyst on the catalytic activity and selectivity were tested to maximize the yield of 4-methoxyphenol. Thus far, 84% selectivity at 95% conversion of hydroquinone was obtained at the optimum reaction conditions (240 °C, reaction with 0.6 g catalyst for 16 h), which was thought to result from the strong basic property and shape selectivity of the Cs ion-exchanged NaX zeolite.

Key words: Alkylation, Methoxyphenol, Hydroquinone, Base Catalyst, Zeolite

INTRODUCTION

Much research has focused on the use of solid acid/base catalysts [Hattori, 1995; Iglesia et al., 1997; Imelik et al., 1985; Kim et al., 2000; Lee et al., 1997; Ono and Baba, 1997; Yoshihiro, 2000] instead of liquid phase catalysts to solve environmental and corrosion problems associated with a homogeneous liquid phase reaction. As well, expensive separation processes and a stoichiometric amount of liquid phase catalysts are not needed in the reactions using solid catalysts. A study of *O*-alkylation reaction of phenol derivatives with methanol was reported recently by Lee et al. [Lee et al., 1998]. In their paper, the reaction, which was conventionally proceeding in the homogeneous liquid phase reaction by using bases such as NaOH and K₂CO₃, was catalyzed by solid base zeolites. Methanol was used instead of DMSA (dimethyl sulfate) as a methylating agent to supply the methyl group. In addition, nearly 100% selectivity to *O*-alkylated product, anisole, was maintained, even at a conversion level higher than 95%. The use of solid catalysts and methanol makes the process economically desirable because they are very simple and inexpensive. Using dimethylcarbonate as a methylating agent, Fu and Ono [Fu and Ono, 1993] reported that a 92% anisole yield was attained over NaX zeolite. In addition, many authors using solid acid catalysts rather than solid base catalysts reported that the main reactions between phenol and alcohol were the ring alkylations which produced cresol or xylenol [Bautista et al., 1993; Samolada et al., 1995; Tleimat-Manzalji et al., 1993].

In this study, *O*-alkylation reaction of hydroquinone was performed by using methanol as a methylating agent in the presence of solid base zeolite catalysts. The effects of basicity of the zeolite and reaction conditions such as temperature, reaction time and the amount of catalyst on the catalytic activity and selectivity were tested to maximize the yield of mono-alkylated product, 4-methoxyphe-

nol. This product is a valuable intermediate for the perfume and flavor industries, especially for food additives like vanillin.

EXPERIMENTAL

1. Preparation of Catalysts

Solid base zeolite catalysts were prepared by three times ion exchanging sodium zeolite (NaX, NaY, Aldrich Chemical Co.) with 0.5 N solutions of alkali metals (K (99+%), Rb (98%)- and Cs (95+%) -acetate, Aldrich Chemical Co.) at room temperature for 48 h. After washing, the samples were dried at 80 °C and calcined at 600 °C for 3 h [Kim et al., 1994]. Nitrogen adsorption isotherms were obtained at 77 K to measure BET surface areas of the samples by using a Micrometrics ASAP 2010 sorption apparatus. The degrees of ion-exchange of the samples were determined by using Varian spectra AA 800 atomic absorption spectrophotometer.

2. Catalytic Activity Measurement

An *O*-alkylation reaction of hydroquinone with methanol was carried out in an autoclave reactor (300 ml) in the temperature range of 200 °C to 300 °C. Before reaction, the catalyst was pretreated at 300 °C for 2 h to remove moisture. After the reactor was charged with the catalyst and the solution of hydroquinone in the excess amount of methanol, nitrogen flow was introduced to the reactor to purge the system and to maintain the initial pressure of the reactor at 150 psia. The mole ratio of methanol to hydroquinone was 1000. The temperature was then increased to the reaction temperature. After reaction for 2 h, the products were analyzed by a gas chromatograph equipped with DB-5 capillary column (J & W Scientific Co. USA) and FID detector, GC-MS (QUATTRO II; VG Co. UK) and NMR (Varian unity plus 300, 500 MHz, Varian Co. USA).

RESULTS AND DISCUSSION

1. Analysis of Products

The conversions and selectivities of the catalysts were calculated

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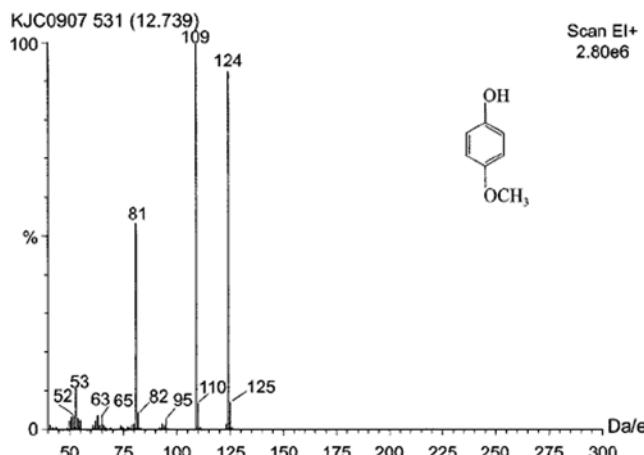
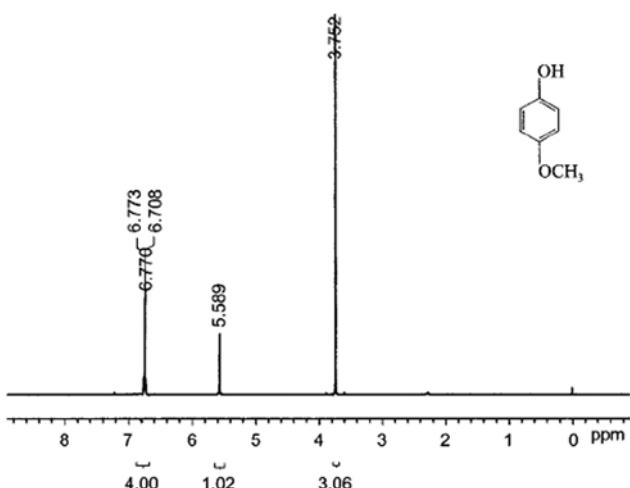


Fig. 1. GC-MS spectrum of 4-methoxyphenol.

Fig. 2. ^1H -NMR spectrum of 4-methoxyphenol.

by using the data obtained from a gas chromatograph and its qualitative analysis was carried out using the GC-MS and NMR. The spectra of the GC-MS and NMR of the main product, 4-methoxyphenol separated from the product mixture are shown in Fig. 1 and 2, respectively. The main product could be distinguished from the by-products such as *C*-alkylated products and 1,4-dimethoxybenzene produced by using the GC-MS peaks at 124 and 109 (without methyl group) in Fig. 1 and the NMR peaks at 6.77 ppm (originated from aromatic ring), 5.58 ppm (from hydroxyl group) and 3.06 ppm (from methyl group) in Fig. 2.

2. Activities of Various Alkali Metal Ion-Exchanged Zeolites in the *O*-Alkylation Reaction of Hydroquinone

The catalytic activities and selectivities of zeolites NaX, NaY and Cs ion-exchanged NaX and NaY in the alkylation reaction of hydroquinone at 260 °C are shown in Fig. 3. Cs ion-exchanged zeolite X shows the highest conversion and selectivity to the mono-alkylated product, 4-methoxyphenol. Considering that X type zeolite has more ion exchangeable sites than Y type zeolite [Breck, 1974] and that Cs ion-exchanged zeolite shows stronger basicity than Na ion-exchanged zeolite [Lee et al., 1998], the higher conversion of NaX than CsNaY indicates that the number of the basic sites as well as the strength of basic site was an important factor in the reaction.

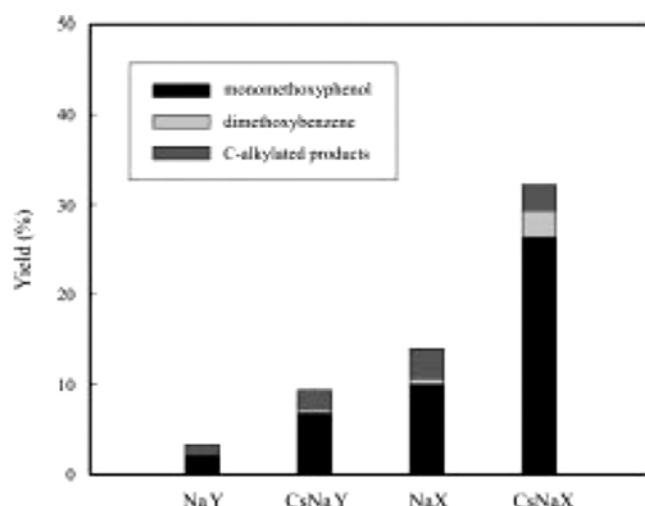
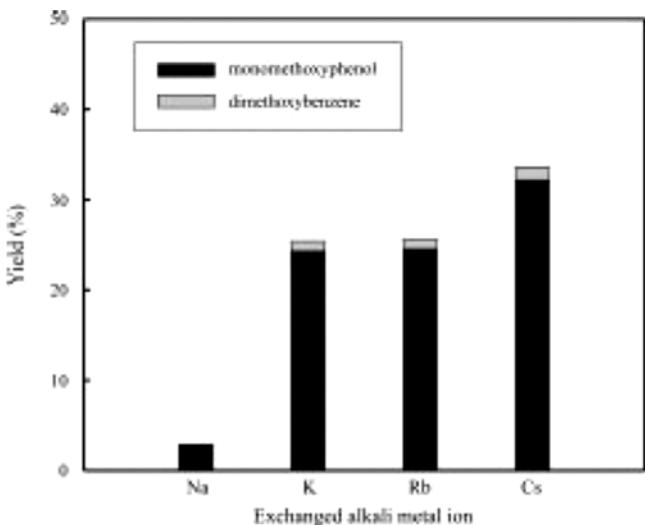
Fig. 3. The catalytic activities of Cs ion-exchanged NaX and NaY zeolites in the *O*-alkylation reaction of hydroquinone with methanol at 260 °C.

Fig. 4. The catalytic activities of NaX zeolites ion-exchanged with various alkali metal ions at 240 °C.

Table 1. Surface areas and composition of zeolite catalysts used in this experiment

Catalyst	BET surface area (m ² /g-cat.)	wt% ^a	Ion-exchange degree (%)
NaX	580	-	-
KNaX	476	10.9	62.2
RbNaX	385	27.6	85.9
CsNaX	345	23.4	46.4

^aDetermined by using an atomic absorption spectrophotometer.

Fig. 4 shows the catalytic activities of NaX zeolites ion-exchanged with various alkali metal ions and Table 1 shows their physical properties such as surface area and ion-exchange degree. In these experiments the reaction temperature was changed from 260 °C to 240 °C and the amount of catalyst was changed from 0.2 g to 0.6 g. As the basicity of the zeolite increased from Na to Cs ion-exchanged

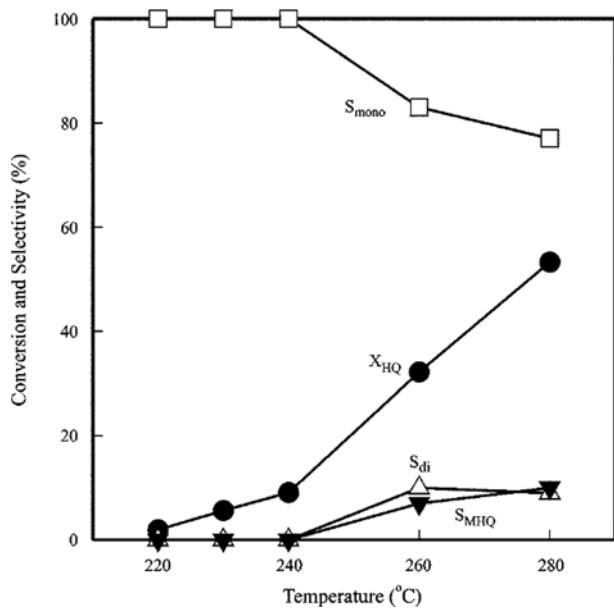


Fig. 5. The effect of reaction temperature on the conversion and selectivities of CsNaX catalyst.

(S_{mono} : selectivity to mono-alkylated product, S_{di} : selectivity to di-alkylated product, S_{MHQ} : selectivity to methylhydroquinone, x_{HQ} : conversion to hydroquinone)

zeolite, the conversion also increased. The conversion level was well correlated with the basicity of the alkali metal ion-exchanged. The main product from the reaction at this temperature was mono-alkylated 4-methoxyphenol. *C*-alkylated products were not detected at 260 °C and thus, higher selectivity to the mono-alkylated product above 95% was obtained at this low temperature. As indicated in the Fig. 4, the by-product mainly produced was a di-alkylated product.

3. The Effect of Reaction Conditions

The conversion of the reaction as a function of the amount of the reactant, hydroquinone at 260 °C was observed in a separate ex-

periment to test the effect of external mass transfer. As the amount of hydroquinone decreased from 1.1 g (0.01 mol) to 0.22 g (0.002 mol) per a fixed amount of methanol (2 mol) and catalyst (0.2 g), the conversion increased linearly, indicating no external mass transfer limitation in three reaction conditions. As a result, 0.002 mol of hydroquinone was used in the following reactions.

The effect of reaction temperature on the conversion and selectivity of CsNaX catalyst was tested as shown in Fig. 5. The conversion of hydroquinone increased with the reaction temperature. In the temperature range between 220 °C and 240 °C, only mono alkylated 4-methoxyphenol was produced. Above 260 °C, the *C*-alkylated product, methylhydroquinone (MHQ) and a di-alkylated product were found while the selectivity to mono-alkylated product decreased to 80%. The conversion and product selectivities as functions of reaction time and temperature are shown in Table 2. As expected, the conversion linearly increased with reaction time at each reaction temperature. However, the selectivity to the mono-alkylated product decreased rapidly when the reaction temperature was higher than 260 °C. At those high temperatures, the selectivities seem to be inversely proportional to conversion. However, at temperatures lower than 240 °C, the selectivity to mono-alkylated product was above 90% even when the conversion increased up to 50%. These results suggest the possibility to the selective production of mono-alkylated 4-methoxyphenol with a high yield by increasing the residence time from 2 h to 10 h at a low temperature.

In Fig. 6, the effect of the loading of CsNaX catalyst on the conversion and selectivity at 260 °C is presented. The conversion increased with the catalyst loading and the selectivity to mono-alkylated product achieved 82% even at 68% conversion over 0.6 g catalyst. The 10% selectivity to *C*-alkylated product over the catalyst of 0.1 g decreased rapidly with increasing the loading amount of the catalyst. As a result, when 0.6 g of the catalyst was used, *C*-alkylated products were not detected. Instead the selectivity to di-alkylated product changed from 9% to 19%. It was reported that *C*-alkylated products from the reaction of phenol and methanol such as cresol and xylenol could be produced over solid acid catalysts

Table 2. The conversions and selectivities of CsNaX catalyst as functions of reaction time and temperature

Reaction temp. (°C)	Reaction time (h)	Conversion (%)	Selectivity (%)			
			Monomethoxy-phenol	Dimethoxy-benzene	Methylhydro-quinone	Unknown byproducts
220	2	1.9	100	0	0	0
	4	3.1	100	0	0	0
	10	7.1	89	0	11	0
240	2	6.5	100	0	0	0
	4	20.1	92	0	8	0
	6	27.9	98	2	0	0
260	2	32.2	83	10	7	0
	4	52.1	82	11	5	2
	6	61.8	77	15	5	3
280	2	94.8	79	15	1	5
	4	53.3	77	9	10	4
	6	81.6	69	20	5	6
		90.2	61	25	6	8

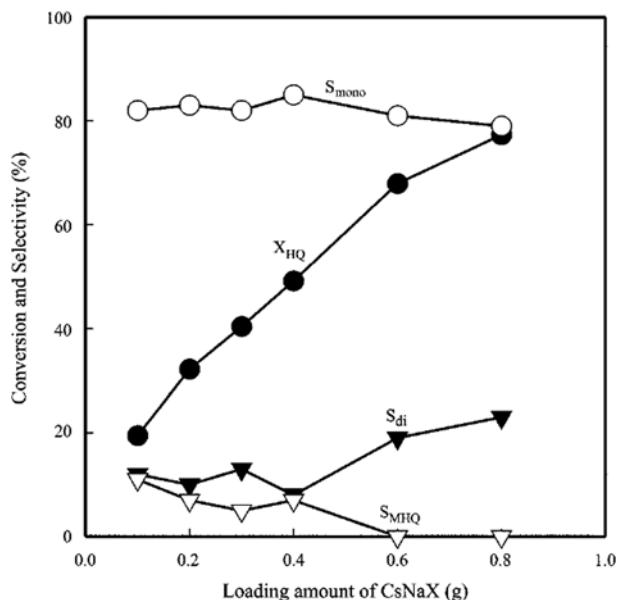


Fig. 6. The effect of CsNaX catalyst loadings on the conversion and selectivities at 260 °C.

[Bautista et al., 1993; Samolada et al., 1995; Tleimat-Manzalji et al., 1993] in addition to *O*-alkylated product (i.e., anisole). Lee et al. [Lee et al., 1998] suggested that the various reaction pathways for the acid catalyst such as decomposition of anisole to phenol and direct ring-alkylation to cresol and methylanisole caused the poor selectivity in the alkylation of phenol. In addition, the high selectivity to anisole over base catalysts was due to the suppression of such side reactions occurring on acid catalysts. However, in the case of hydroquinone, the *C*-alkylated product, 2-methylhydroquinone, was always detected at above 260 °C.

Even though the reaction mechanism of *C*-alkylation at high temperatures and short residence times with a small loading of catalyst is not explained well, it is clear that production rate of *C*-alkylation products decreases rapidly with lowering the reaction temperature or increasing the loading of catalyst. The basic nature of Cs ion-exchanged zeolite is considered to be responsible for these results. In other words, the increase in the contact time by increasing the catalyst loading or the decrease in the reaction temperature promotes the rate of *O*-alkylation reaction compared to that of *C*-alkylation reaction. This is because *O*-alkylation reactions prevail on the basic catalysts. In addition, this reasoning can be inferred from the results represented in Fig. 3, because zeolite X has larger number of basic sites than zeolite Y has.

Another interesting fact observed in this reaction is the high selectivity to the mono-alkylated product even at high conversion. Because the di-*O*-alkylated product is obtained from the mono-alkylated product by further *O*-alkylation reaction, it was expected that the selectivity to the mono-alkylated product would be inversely proportional to the conversion. However, a high selectivity to mono-alkylated product even at high conversion levels was observed in Table 2. This trend may be due to the diffusional limitation of the mono-alkylated product in zeolite pores.

4. Optimization of the Reaction Conditions to Maximize the Yield of Mono Alkylated 4-Methoxyphenol

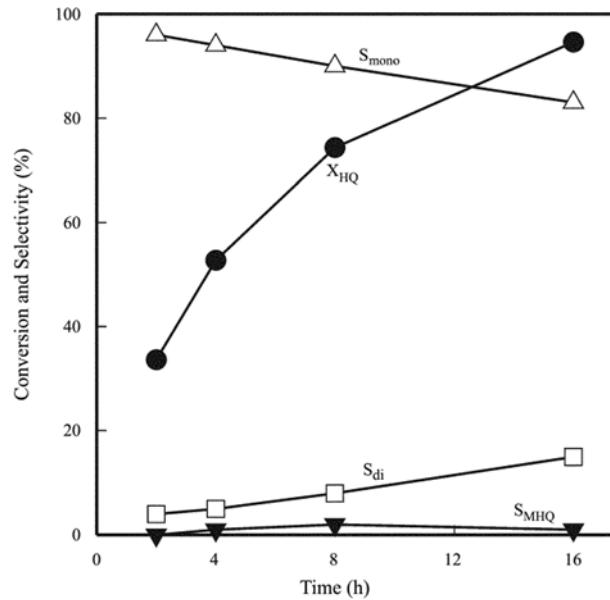


Fig. 7. The conversion and selectivities of CsNaX catalyst as a function of the reaction time at 240 °C.

To produce 4-methoxyphenol selectively without the production of *C*-alkylated products, the optimum reaction conditions were deduced from the experiment results. 0.002 mol of hydroquinone was reacted with 2 mol of excess methanol over 0.6 g of the catalyst at 240 °C. In Fig. 7, the conversion (X_{HQ}) and selectivity to mono-alkylated products (S_{mono}) as a function of the reaction time are shown. By increasing the reaction time to 16 h, conversion increased to 95%. The selectivity to *C*-alkylated product (MHQ) was less than 1% even at a conversion level of 95%. 96% selectivity to mono-alkylated product was obtained at 34% conversion, while the selectivity decreased to 84% with increasing conversion to 95%, whereas the selectivity to the di-alkylated product increased to 15%. In a separate experiment, it was confirmed that the mono-alkylated 4-methoxyphenol reacted with methanol to make di-alkylated product even though the reaction rate was partially affected by the diffusional limitation in zeolite pores. This indicates that the yield showed the maximum and that the optimum conditions for the maximum yield of 4-methoxyphenol had to be determined kinetically.

SUMMARY

An *O*-alkylation reaction of hydroquinone with methanol was performed by using alkali metal ion-exchanged zeolites to produce mono *O*-alkylated 4-methoxyphenol selectively. The catalytic activities of the zeolites are well correlated with the number of basic sites. *C*-alkylated methylhydroquinone was produced at above 260 °C, but its production rate decreased rapidly with decreasing the reaction temperature below 240 °C and increasing the loading of catalyst. Thus far, 84% selectivity to 4-methoxyphenol at 95% conversion of hydroquinone has been obtained at the optimum reaction conditions. Strong basicity of the zeolite catalysts promoting *O*-alkylation reaction rather than *C*-alkylation reaction at low temperatures and the diffusional limitation of the mono-alkylated product in zeolite pores are responsible for the high selectivity to 4-methoxyphenol, the intermediate product in the series reaction.

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