The effect of phase transition of methanol on the reaction rate in the alkylation of hydroquinone

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Abstract−An O-alkylation reaction of hydroquinone with excess methanol was carried out by using alkaline metal ion-exchanged zeolite catalysts at various phases of methanol in a slurry type reactor. The amount of methanol, used as a methylating agent and also a solvent, significantly affected the reaction rate. When the amount of methanol was decreased from 2 mol to 0.6 mol, the reaction rate was increased more than nine times. These changes in the reaction rate could be explained by the pressure change and the phase transition of the reactant, methanol, depending on the temperature and the elimination of a diffusion limitation of reactants through the zeolite pores in a gas phase condition. Thus, higher than 89% selectivity to 4-methoxyphenol was obtained at 80% conversion of hydroquinone at a gas phase reaction condition using 1 mol of methanol for 2 hours.

Key words: Alkylation, Hydroquinone, Methanol, Phase Transition

INTRODUCTION

4-Methoxyphenol, which is a mono-alkylated product to be made by alkylation reaction of hydroquinone, is a valuable intermediary for the perfume and flavor industries and food additives. O-alkylation reactions of hydroquinone to make mono- or di-alkylated products are usually performed by using methylating agents such as methanol, dimethyl sulfate and dimethyl carbonate in the presence of solid or liquid phase basic catalysts [1-5]. However, several disadvantages such as corrosion and environmental problems are associated with the use of a liquid phase catalyst [6]. Furthermore, expensive separation processes and a large stoichiometric amount of liquid base are needed in a liquid type of reaction. Much research has been concentrated on the use of solid basic catalysts [7-13] instead of liquid phase catalysts. In addition, the use of methanol as a methylating reactant and solvent to dissolve a reactant with a high boiling point like hydroquinone is desirable because it is inexpensive and makes the system simple in such an alkylation reaction.

During the tests of the activities of the solid base zeolite catalysts in the O-alkylation reaction of hydroquinone with methanol, it was found that the amount of methanol seriously affected the reaction rate. An increase in the reaction rate of more than five times without much variation in selectivity to a mono-alkylated intermediate product in the series reaction has not been reported previously when the excess amount of methanol was decreased.

In this work, the details of the experimental results are described and the cause of this phenomenon is explained by the facts related to phase transitions along with pressure changes and modification of transport properties of reactants and products through the pores of zeolites in various phases of methanol.

EXPERIMENTAL

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1. Catalyst Preparation

Solid base zeolite catalysts were prepared by three times ion-exchanging procedure of a sodium zeolite (NaX, 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 hours. After washing, the samples were dried at 80 °C for 24 hours and calcined at 600 °C for three hours [14].

2. Reaction Procedures

An alkylation reaction of hydroquinone with methanol was carried out in an autoclave reactor (300 ml) in the temperature range of 200 to 300 °C. Before reaction, the catalyst was pretreated at 300 °C for two hours to remove moisture. After the reactor was charged with 0.2 g of the catalyst, hydroquinone was dissolved by the excess amount of methanol and nitrogen flow was introduced to the reactor to purge the system and to maintain the initial pressure of the reactor between 0 and 500 psig. The mole ratios of methanol to hydroquinone used ranged from 100 to 1,000. The temperature was then increased to the reaction temperature. After reaction for two hours, the reactor was cooled to room temperature for sampling the products. The products were analyzed by a gas chromatograph equipped with DB-5 capillary column (J & W Scientific) and FID detector.

RESULTS AND DISCUSSION

1. The Effect of the Amount of Methanol

Fig. 1 shows the activity and selectivity of cesium ion-exchanged zeolite (CsNaX) as a function of the amount of methanol used with 0.22 g of hydroquinone under 150 psig of the initial pressure at 240 °C. As shown in Fig. 1, the conversion of hydroquinone rapidly increased when the amount of methanol was decreased from 2 mol to 0.6 mol at 240 °C. In particular, when 0.6 mol of methanol was used, 93% of the conversion was obtained though 10% of the conversion when 2 mol of methanol was used in the same condition. It is indicated that the reaction rate when 0.6 mol of methanol was used increased
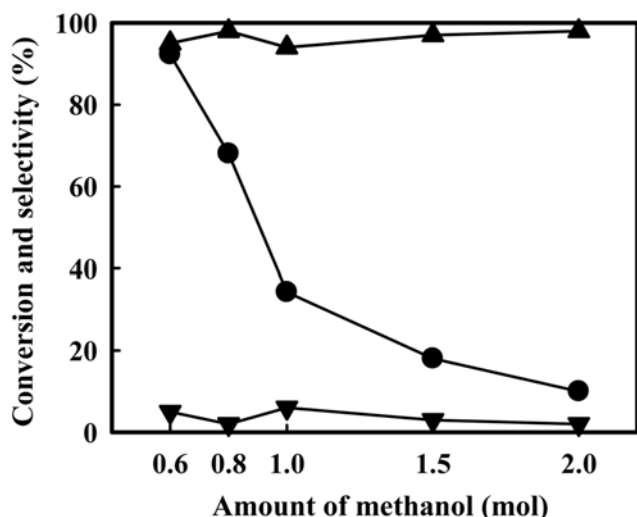
Fig. 1. The catalytic activity and selectivity of cesium ion-exchanged zeolite in the methylation reaction of hydroquinone with methanol as a function of the amount of methanol used at 240 °C with 150 psig initial pressure: ●: Conversion of hydroquinone; ▲: Selectivity of mono-alkylated product; ▼: Selectivity of di-alkylated product.

Table 1. The reaction rate by adjusting the amount of methanol

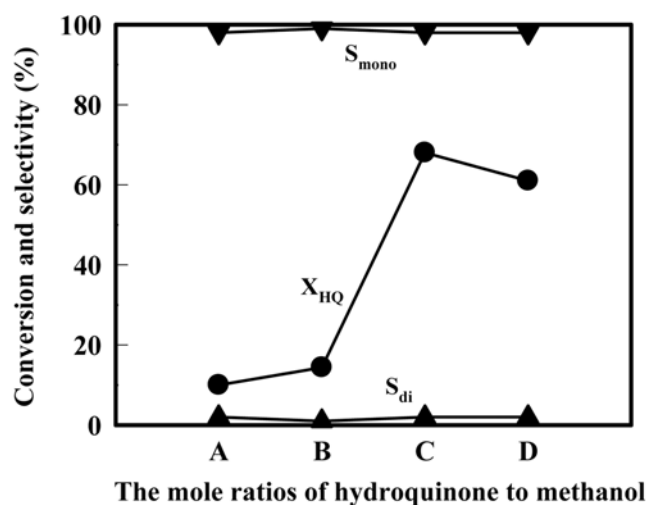| The amount of methanol (mol)	The reaction rate (mol/s·$g_{catalyst}$)
2	1.39×10^{-7}
1.5	2.50×10^{-7}
1	4.75×10^{-7}
0.8	9.44×10^{-7}
0.6	1.28×10^{-6}

Fig. 2. The catalytic activity and selectivity as a function of the mole ratios of hydroquinone to methanol: A, MeOH/HQ=1,000 (2 mole/0.002 mole); B, MeOH/HQ=400 (2 mole/0.005 mole); C, MeOH/HQ=400 (0.8 mole/0.002 mole); D, MeOH/HQ= 200 (0.8 mole/0.004 mole).

more than nine times when 2 mol of methanol was used as shown in Table 1. Also, the high selectivity to the mono-alkylated product
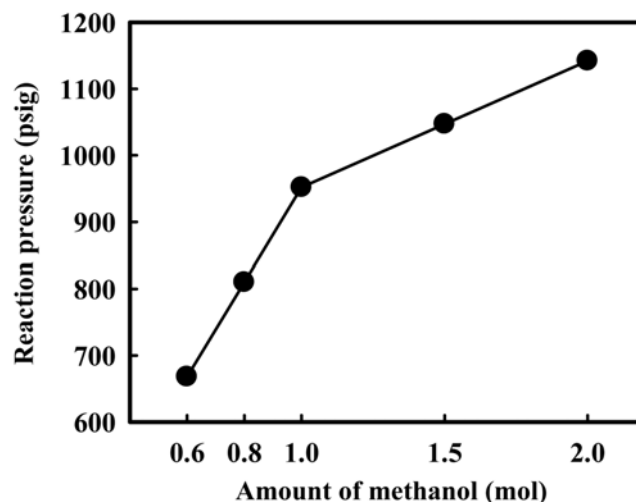
Fig. 3. The reaction pressure in the reactor as a function of the amount of methanol with 0.22 g of hydroquinone and 0.2 g of catalyst at 240 °C.
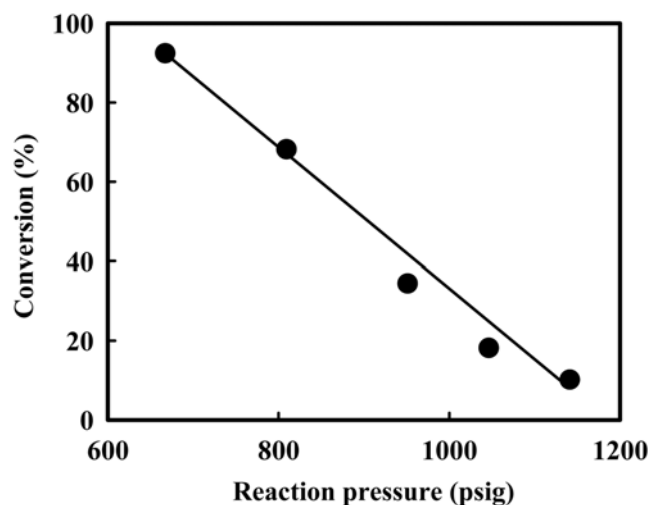

Fig. 4. The conversion of hydroquinone as a function of the reaction pressure in the same conditions as in Fig. 3.

(4-methoxy phenol) even at a conversion level of about 93% was maintained.

To investigate the effects of amounts of reactants and mass transfer limitation, the catalytic activity and selectivity at different mole ratios of hydroquinone to methanol from 1/1000 to 1/200 were tested. In the experiments, the weight ratio of the amount of catalyst to that of hydroquinone was fixed at 1. As shown in Fig. 2, the reaction rate was very dependent on the amount of methanol. It was the amount of methanol rather than the ratio of hydroquinone to methanol that affected the reaction rate. This result was thought to be due to the change of the reaction pressure by the amount of methanol.

The effect of the reaction pressure on the conversion was tested. Fig. 3 shows the reaction pressure as a function of the amount of methanol. The reaction pressure gradually decreased with decreasing the amount of methanol from 2.0 mol to 1.0 mol and rapidly decreased with decreasing from 1.0 mol to 0.6 mol.

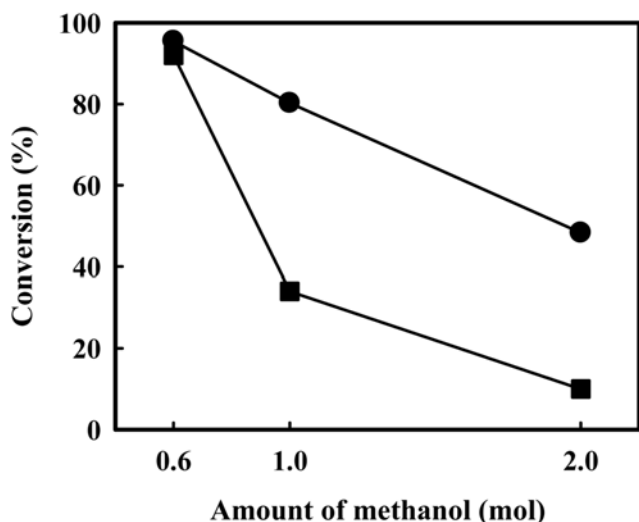However, as shown in Fig. 4, the conversion is inversely propor-

Fig. 5. The catalytic activity of cesium ion-exchanged zeolite in the methylation reaction of hydroquinone with methanol as a function of the amount of methanol used at 240 ℃ with/without 150 psig initial pressure: ●: Conversion of hydroquinone without initial pressure; ■: Conversion of hydroquinone with 150 psig initial pressure.

Fig. 7. The activities of various alkali metals loaded zeolite 13X at 240 ℃: ●: 2 mol methanol with 150 psig initial pressure; ■: 0.6 mol methanol with 150 psig initial pressure; ▲: 0.6 mol methanol without initial pressure.

tional to reaction pressure by changing the amount of the methanol from 0.6 mol to 2 mol. These results indicate that the reaction rate could be changed dramatically depending on the reaction pressure originating from vaporization of methanol or initial nitrogen charge. Fig. 5 shows the effect of the initial pressure on the catalytic activity with/without 150 psig of the initial pressure with the amount of methanol from 2.0 mol to 0.6 mol at 240 ℃. As shown in Fig. 5, all the conversions without 150 psig of the initial pressure under the amount of methanol from 2.0 mol to 0.8 mol were much higher than these with the initial pressure.

To confirm that the conversion depends on the reaction pressure

in detail, the activity of the catalyst was compared under the circumstances for each similar reaction pressure, adjusted by the amount of methanol or the initial pressure. These results are shown in Fig. 6. The reaction pressures were changed by the various amounts of methanol such as 1, 1.5 and 2 mol and by various initial pressures such as 0, 100, and 150 psig under 1 mol of methanol, respectively. As shown in Fig. 6, both results are well matched. It was concluded that the reaction pressure is a very important factor for the catalytic activity.

Fig. 7 shows the effects of the amount of methanol and the reaction pressure on the conversion over various catalysts such as NaX, KNaX, RbNaX and CsNaX. The catalytic activities of all of the catalysts increased with decreasing the amount of methanol or without the initial pressure of N_2. These results indicate that the reac-
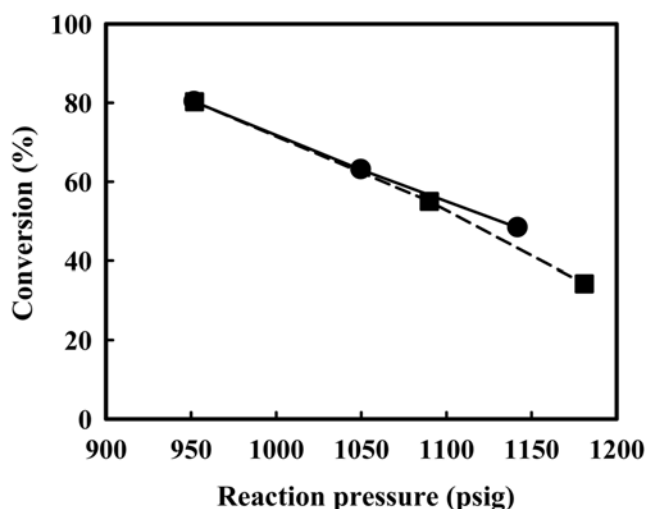

Fig. 6. The catalytic activity as a function of the reaction pressure by adjusting amount of methanol or initial pressure: ●: 1, 1.5, 2 mol methanol without initial pressure; ■: 0, 100, 150 psig initial pressure using 1 mol methanol.
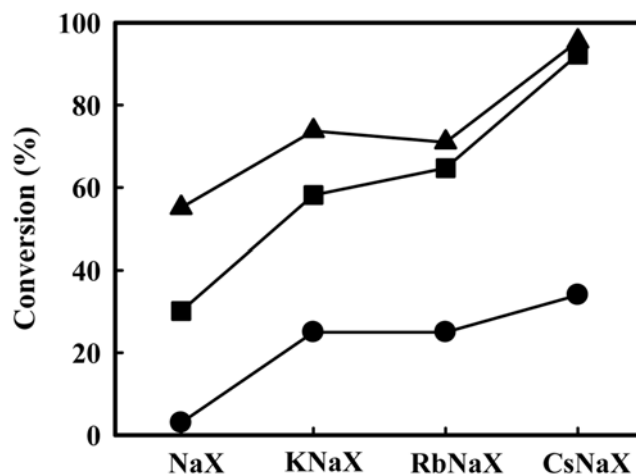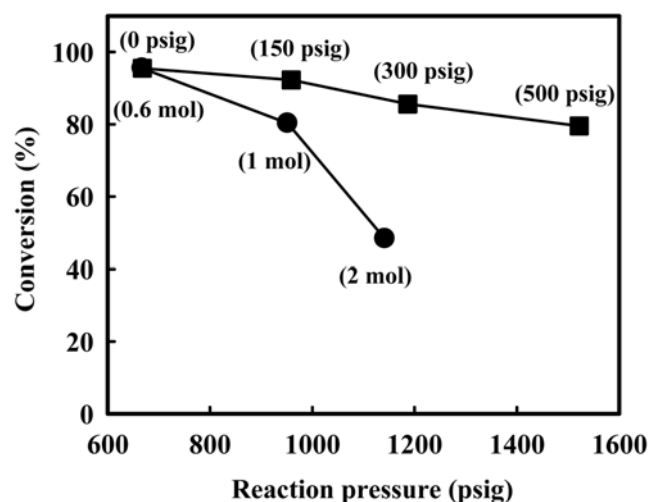

Fig. 8. The catalytic activity as a function of the reaction pressure adjusted by the amount of methanol or initial pressure: ●: 0.6, 1, 2 mol methanol without initial pressure; ■: 0, 150, 300, 500 psig initial pressure using 0.6 mol methanol.
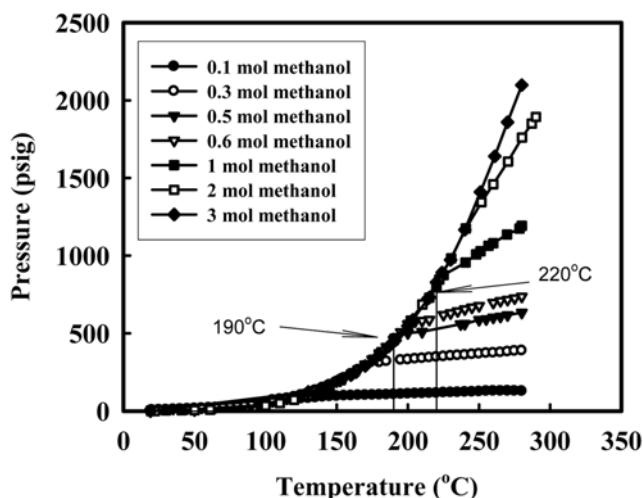
Fig. 9. The relation of the temperature and the amount of methanol on the pressure in the reactor without initial pressure.
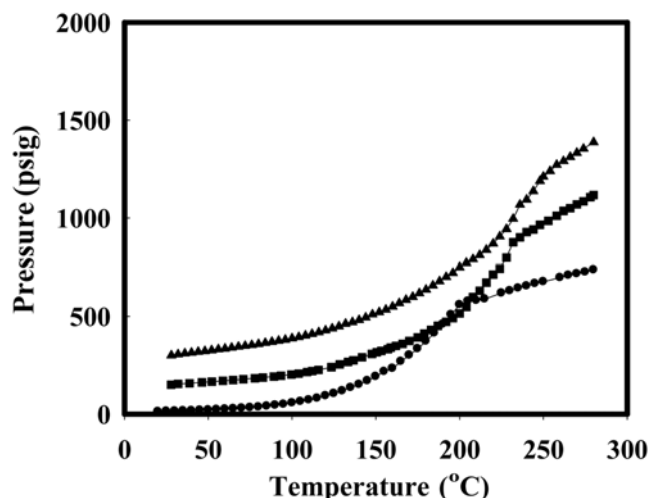

Fig. 10. The relation of the temperature and the initial pressure on the pressure in the reactor using 0.6 mol methanol: ●: 0 psig; ■: 150 psig; ▲: 300 psig initial pressure.

tion pressure plays an important role in the reaction regardless of the catalysts such as NaX, KNaX, RbNaX and CsNaX.

2. The Effect of Phase Transition

Fig. 8 shows the catalytic activity as a function of the reaction pressure adjusted by the amount of methanol or the initial pressure. When the reaction pressures were increased by increasing the amount of methanol from 0.6 mol to 2.0 mol without the initial pressure, the conversion rapidly decreased from 96% to 48%. But in the case of the changes of the initial pressure from 0 psig to 500 psig using 0.6 mol methanol, the conversion slowly decreased from 96% to 82%. Compared to the results shown in Fig. 6, these different results with 0.6 mol of methanol indicated that a new factor in addition to the reaction pressure had to be considered in this reaction condition.

So, the effects of temperature and the amount of methanol on the pressure of the reactor used in this system were checked as shown in Fig. 9. When 1 mol of methanol was used without initial pressure of N_2, the pressure was increased along the equilibrium line initially up to 220 °C when temperature was increased. However, the pressure increased with a different slope lower than that of the equilibrium line after 220 °C. When 0.5 mol methanol was used, the secession temperature separated from the equilibrium line was decreased to 190 °C and the slope itself diminished. It was indicated that the phase before the secession temperature was a liquid or a liquid-vapor phase and after the secession temperature it was a gas phase. The slow increase in pressure after secession temperature was due to the volume expansion of the gas phase.

When 2 mol and 3 mol of methanol were used, the pressures developed by the methanol in the reactor at 240 °C were about 1,200 psig and the pressure continuously increased when temperature increased. No difference between the reactor pressures and the equilibrium line above 2 mol of methanol indicated that the liquid-gas equilibrium phase was maintained in the reactor. When 1 mol, 0.8 mol and 0.6 mol of methanol were used, the pressures in the reactor at 240 °C were reduced to 900, 800 and 700 psig, respectively. These pressure drops indicated that all of the methanol in the reactor at the temperature was in gas phase. As shown in Fig. 10, it was confirmed that the secession temperature of the equilibrium line of

0.6 mol of methanol under the initial pressure of 300 psig was below 240 °C. Also, these results indicated that the enhanced reaction rate was obtained under gas phase rather than under liquid-vapor equilibrium phase. The enhanced reaction rate can be explained by the faster diffusion rate of the molecules in gas phase developed by phase transition from liquid than that in the liquid-vapor equilibrium phase.

CONCLUSIONS

An O-alkylation reaction of hydroquinone with methanol was performed by using alkali metal ion-exchanged zeolites to produce 4-methoxyphenol. In conclusion, higher than 89% selectivity to 4-methoxyphenol was obtained at 80% conversion of hydroquinone at gas phase reaction condition. The amount of methanol which was used as a methylating reactant and a solvent affected the reaction rate through the controls of the reactor pressure and phase transition. So the reaction rate could be increased by decreasing the reaction pressure and phase transition from liquid to gas, which is a very different situation found in a general slurry type reactor. The reaction rate in gas phase of methanol was faster than that in liquid-vapor equilibrium phase, which was due to the faster diffusion rate of the reactant in gas phase than that in liquid-vapor equilibrium phase.

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