Alkylation of Phenol with Cyclohexene*

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Summary: The alkylation of phenol with cyclohexene in the vapor phase has been studied over the cation-exchanged X zeolite catalysts. Because of the dealkylation of products, the catalytic activity decreased with rising reaction temperature. The yield of cyclohexylphenol increased linearly with increase in the amount of acid. Furthermore, the catalytic activity decreased by the addition of pyridine. However, the order of catalytic activity for alkylation of phenol with cyclohexene was not in accord with that for the cracking of cumene. On the other hand, the volcanoshape relation was observed between the catalytic activity for alkylation of phenol with cyclohexene and the electronegativity of metal ion in the catalyst. On the basis of these results, it is concluded that the alkylation reaction proceeds on the acid sites, and the active sites are the surface protons and the metal ions of the catalyst.

1 Introduction

It is known that synthetic zeolites are versatile catalysts for various reactions^{1),2)}. The catalytic properties of cation-exchanged zeolites X and Y have been discussed by many workers for alkylation of phenol with a variety of alkylating reagents³⁾. However, studies on the alkylation of phenol with cycloolefin are very scanty. Cyclohexylphenol has been used as an intermediate for insecticides disinfectants, medicines, and it is manufactured by alkylation of phenol with cyclohexylchloride or cyclohexene in the liquid phase⁴).

In this paper, we have studied alkylation of phenol with cyclohexene over the cation-exchanged X zeolites, the active sites of zeolites, and the mechanism of this reaction.

2 Experimental

2.1 Preparation of Catalysts

The cation-exchanged zeolite catalysts were prepared by exchange with exess of aqueous solution of the desired metal chloride at 80°C for 10 hours. All cation-exchanged zeolite catalysts dried at 120°C were calcined at 500°C for 3 hours. The degree of cation exchange was determined by atomic absorption spectrometry.

2.2 Aparatus and Procedure

Catalytic activity measurements were made in

a fixed bed reactor at atmospheric pressure. The calcined catalyst was placed in the electrically heated pyrex glass reactor having a diameter of 18 mm. A mixture of phenol and cyclohexene was fed into the catalyst bed by a microfeeder. Samples of the products were collected for analysis using an ice trap. The chosen standard conditions were as follows;

W/F=117.6 g·hr/mol Cyclohexene (CYH)/PhOH (molar ratio)=1.0 Reaction temperature: 310° C Carrier gas: N₂ Flow rate of carrier gas: 150 ml/min

The reaction products were analyzed by gas chromatography using a 2 m column filled with stationary phase Chromosorb W ($60 \sim 80$ mesh) containing 10% SE-52. The flow rate of the carrier gas was 40 ml/min and analytical temperature was 190°C. The main products were cyclohexylphenol (CHP) isomers. A small amount of by-product was obtained, and it was in accord with that obtained by heating cyclohexene alone. Mixtures of para and ortho isomers were analyzed under the same conditions after they were acetylated⁵.

2.3 Determination of Solid Acidity and Other Physical Properties

The amount and strength of acid were determined by the *n*-butyl amine titration method⁶). The physical properties of catalysts and materials adsorbed on the catalysts were determined by thermal analysis and infrared absorption.

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Fig. 1 Activity Change with Time on Stream for Alkylation of Phenol with Cyclohexene : (●) MnX, (●) MgX, (●) CaX, (⊖) CoX, (◎) SrX, (•) BaX, (○) ZnX



Fig. 2 Effect of Contact Time on Alkylation of Phenol with Cyclohexene : Reaction temperature=310°C, Catalyst : MgX, (○) total CHP, (●) o-CHP, (○) p-CHP, (●) m-CHP

3 Results and Discussion

3.1 Effects of W/F and Reaction Temperature

The effects of W/F and reaction temperature were studied as regards the proton-exchanged X zeolite (HX) and Mg ion-exchanged N zeolite (MgX).

Catalytic activity changed gradually with time on stream as shown in **Fig. 1**. The data were taken at 1 hour after on stream when the yield of aromatic products was usually highest.

The effect of W/F is shown in **Fig. 2**. W/F is defined as follows;



Fig. 3-a Effect of Reaction Temperature on Alkylation of Phenol with Cyclohexene : W/F= 117.6 g ·hr/mol, Catalyst : HX, (○) total CHP, (●) o-CHP, (●) p-CHP, (●) m-CHP



Fig. 3-b Effect of Reaction Temperature on Dealkylation of o-CHP : W/F=0.6 g hr/mol, Catalyst : HX

$$W/F = \frac{\text{weight of catalyst (g)}}{\text{feed rate (mol/hr)}}$$

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Figure 2 shows that the highest yield of CHP is obtained at $W/F \ge 92.0$. Above 92 there is no remarkable change in the yields of products. Figure 3-a shows the effect of reaction temperature on yield and selectivity. It is clear that the total yield and selectivity of *o*-CHP decrease with increasing reaction temperature; nevertheless the selectivity of *p*-CHP maintains its constancy. The cause of the decrease in the total yield is considered as follows:

(1) The coating of the surface of catalysts with by-products formed from the cracking of CYH

Cation	Exchanged (%)	Yield (%)	Selectivity		
			o-CHP	<i>p</i> −CHP	m-CHP
Na		1.7	0.61	0.29	0.10
Ba	32.4	5.0	0.64	0.31	0.05
Sr	46.5	6.5	0.63	0.28	0.09
Ca	44.0	9.4	0.44	0.32	0.24
Mg	29.8	10.9	0.43	0.32	0.25
Mn	32.7	13.3	0.44	0.31	0.25
Zn	46.9	11.0	0.36	0.26	0.38
Co	35.4	8.6	0.42	0.28	0.30
Cr	48.0	1.1	0.41	0.29	0.30
н	36.5	12.0	0.45	0.29	0.26
SiO ₂ -Al ₂ O ₃	_	10.3	0.38	0.22	0.40
Āl₂O₃	—	12.4	0.63	0.21	0.16

Activity and Analysis of Exchanged X Table 1 **Zeolites**

(2) Dealkylation of aromatic products, i.e., mixtures of o-, m- and p-CHP

Figure 3-b shows the effect of reaction temperature on the dealkylation of o-CHP. Dealkylation reaction becomes more active with rising temperature. On the other hand, there is no remarkable change in the yields of by-products. These results indicate that the decrease in the total yield with increasing temperature is due to the dealkylation of CHP.

3.2 Order of Catalytic Activity

Table 1 shows the kind of catalyst, the degree of cation exchange, the catalytic activity and the selectivity of CHP. The order of catalytic activity is as follows;

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MnX>HX>ZnX, MgX>CaX>CoX>SrX
>BaX>NaX, CrX
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Furthermore, the catalysts used are classified into the following three types

(1) o-CHP \gg p-CHP \gg m-CHP ·····NaX, BaX, SrX, Al₂O₃ o-CHP>p-CHP>m-CHP (2)

······CaX, MgX, MnX, HX

(3)
$$m$$
-CHP> p -CHP
.....ZnX, CoX, CrX, SiO₂-Al₂O₃

Judging from the above results, the catalytic activity and selectivity are probably related to the nature of the metal ions in the catalysts. 3.3 Relationship between Amount of Acid and Catalytic Activity

Data regarding acidity are shown in Fig. 4. The catalysts used are solid acid with $H_0 \ge$ -3.0 with exception of ZnX (H_c ≥ -5.6). The amount of acid of ZnX is more than that of SiO₂-Al₂O₃. Since CoX and CrX were colored, we did not measure the acidity of these catalysts. Figure 5 shows the linear relationship between



Fig. 4 Acid Content vs. Acid Strength for Cation-Exchanged X Zeolite Catalysts Heated at $500^{\circ}C:(\bigcirc)$ ZnX, (\bigcirc) MnX, (**●**) MgX, (()) CaX, (()) SrX, (() BaX, (\ominus) SiO₂- Al_2O_3 , (()) HX



Fig. 5 Catalytic Activity for Alkylation of Phenol with Cyclohexene as a Function of Amount of Acid $(H_0 \leq +4.8)$

the total amount of acid ($H_0 \leq +4.8$) and catalytic activity. The catalytic activity decreased by the addition of pyridine, and the catalytic activity of Al₂O₃ was poisoned by NaOH or Ca(OH)₂. These results show that the alkylation proceeds on the acid sites, and the selectivity of CHP is related to acid strength. In the case of using catalysts with weak acid strengths, the mixture was rich in ortho isomer, while in the case of using catalysts with strong acid strengths, the mixture was rich in meta isomer. A similar relationship was observed in the alkylation of phenol with alcohols⁷). Figure 6 shows that the total amount of acid increases with increasing electronegativity of the metal ion⁸⁾ in the catalysts. This result supports Ward's suggestion that

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Fig. 6 Relationship between Amount of Acid (H₆≤ +4.8) and Electronegativity of Metal Ions in the Catalysts



Fig. 7 Activity Change with Time on Stream for Cracking of Cumene : W/F=0.52 g·hr/mol, Reaction temperature : 450°C

acid sites are formed by a fission of adsorbed water under the influence of the electrostatic field⁹⁾.

3.4 Cracking of Cumene

The nature of active sites on zeolites has been studied by many workers^{10),11)}. Ward has reported the infrared spectra of pyridine adsorbed on the transition metals and the alkaline earth metal ion exchanged X zeolite. According to his study, these catalysts have only Brönsted acidity. If the active sites of the catalysts used in this alkylation study are the Brönsted sites, the order of catalytic activity should be in accord with that for cumene cracking^{12),13)}. So we also studied cumene cracking over the same catalyst used in this alkylation study. **Figure 7** shows the change of catalytic activity for cumene



Fig. 8 DTA and TGA Curves : (A) Fresh ZnX Impregnated with Organic Compound; Used Catalysts in alkylation : (B) NaX, BaX, SrX, (C) MgX, MnX, (D) ZnX, CoX

cracking with time on stream. The catalysts used are classified into the following two types;

- (1) One type shows the decrease in catalytic activity.....ZnX, CoX, CrX, SiO₂-Al₂O₃
- (2) The other type shows constant catalytic activity.....BaX, SrX, CaX, MgX, MnX, Al₂O₃

From this result, the type (1) is considered to have strong acid sites. The order of initial activity for cumene cracking is as follows;

$$ZnX > HX > MnX > MgX > CoX > CrX$$

> $CaX > SrX > BaX > NaX$

This order is not in accord with that of activity for the alkylation reactions. The above results suggest that the active sites for alkylation are not only the Brönsted sites but also the other positive sites, perhaps metal ions, that contribute to the activity.

3.5 Adsorption

The catalytic activity for alkylation changed gradually with time on stream. The stronger the acidity of the catalyst was, the more remarkable was the decrease of activity. After the alkylation reaction, the surface became black. On exposure to the air at 500°C, the color of the surface turned to the original color. The color change is probably due to the deposition of carbon. Figure 8 shows the results of thermal analysis of the catalysts used in the alkylation and the fresh ZnX impregnated with CYH, PhOH and CHP. Figure 8 shows one or two exothermic peaks. Accordingly acidity of the catalyst became stronger and the exothermic temperature became higher. DTA and TGA of used catalyst are in accord with those of the fresh catalysts impregnated with o-CHP. The thermal analysis of the catalysts used in the isomerization reaction of o-CHP is also in accord with the results shown in Fig. 8. The burning temperature of one component is expected to be constant so far as the DTA conditions such as velocity of air and rate of raising temperature are concerned. Referring to this expectation, it is possible that CHP remains on the surface of the catalyst. The existence of CHP was further investigated by infrared analysis. Prior to infrared analysis, the catalyst used in the alkylation was calcined at 310°C for 1 hr under the current of N_2 (flow rate: 150 ml/min). The infrared spectra of the catalyst using KBr method are shown in Fig. 9. The absorption at 1,450 cm⁻¹ is due to CH and CH_2 deformation band. The absorption at $2,920 \text{ cm}^{-1}$ is due to the CH stretching band, and the absorption at 1,495 cm⁻¹ and 1,595 cm⁻¹ are due to the inplane vibration of the benzene ring. Also the spectra of fresh ZnX impregnated with CYH, phenol and CHP, respectively, were taken for comparison with the spectra shown in Fig. 9. Prior to infrared analysis, the samples impregnated with phenol and CHP were dried at 100°C in the air, while the sample impregnated with



Fig. 9 Infrared Spectra : (A) Fresh catalyst, (B) Used ZnX in Alkylation

CYH was air-dried at room temperature owing to the thermally instability of CYH. The absoprtion at 2,920 cm⁻¹ and 2,860 cm⁻¹ in Fig. 9 were recognized also in the spectra of fresh ZnX impregnated with CHP, while in the spectra of the sample impregnated with phenol they were not recognized. Further, the absorption at 1,450 cm⁻¹ was found in the sample impregnated with CHP, and the absorption at 1,470 cm⁻¹ was found in the sample impregnated with phenol. The former absorption coincided much more closely with that of used ZnX as regards the position of absorption. The spectra of the sample impregnated with CYH were markedly more different as a whole from the spectra of used ZnX. From these infrared spectra and thermal analysis, it may be clear that CHP remains on the surface of the catalyst. This CHP may be desorbed slowly from the active site, and fresh phenol may occupy the recovered site in place of CHP owing to the similarity of the adsorption behavior.

3.6 Relationship between Catalytic Activity and Electronegativity

From the relationship between the catalytic activity and the acidity, it is clear that this alkylation proceeds on the acid sites. The acid sites are considered to be formed by the polarization of metal ions in the catalyst. We have discussed the relationship between catalytic activity and electronegativity of metal ion. **Figure 10** shows the volcano shape relation. There have been many examples of volcano shape relationship between catalytic activity and electronegativity



Fig. 10 Relationship between the Catalytic Activity for Alkylation of Phenol with Cyclohexene and the Electronegativity of Metal Ion in Cation-Exchanged X Zeolite

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of metal ion or the heat of formation of the intermediate¹⁴)⁻¹⁶). A cause of these volcano shape relationships has been considered as follows;

(1) Since the active sites of the catalysts on the right hand are different from those on the left hand in **Fig. 10**, the reaction mechanism for each catalyst differs.

(2) The rate-determining step on the right hand is different from that on the left hand. In this paper, we have discussed the cause of volcano shape relation for this type of alkylation. The results of cracking of cumene suggest that the active sites are the Brönsted sites and metal ions in the catalyst. Changes in the kind of products were not observed for all catalysts. Furthermore, the catalysts on the left hand have weak acid sites and those on the right hand have strong acid sites. The rate of adsorption or desorption of CHP is changed by the strength of the acid sites. The discussion suggests that the volcano shape relation is probably due to the difference in the rate-determining step. 3.7 Estimation of Reaction Mechanism

We have discussed isomerization of o-CHP over the zeolite catalysts. As shown in **Table 2**, while the dealkylation reaction mainly occurs, the isomerization hardly takes place. In the case of zeolite catalysts, the reaction takes place within the super cage of the zeolite crystal as reported by many workers¹⁷). It is assumed that the occurrence of the movement of the cyclohexyl group within the super cage would be difficult. Thus, the isomerization reaction would be probably depressed, and the alkylating reagent would directly attack the benzene ring of phenol. Since the active sites of X zeolites

Table 2 Reaction of o-Cyclohexylphenol

Catalyst	Conversion (%)	Selectivity		
		Dealkylation	Isomerization	
SrX	61.4	0.94	0.06	
CaX	47.1	0.90	0.10	
HX	87.0	0.88	0.12	
HY	63.6	0.89	0.11	
[Al ₂ O ₃	94.3	0.93	0.07	
TiO ₂	trace	trace	-	

 $W/F=0.6 g \cdot hr/ml$. Reaction temperature : 300°C

are acid sites and metal ions, it seems reasonable to assume that the reaction mechanism of alkylation of phenol with CYH is shown below.

The estimation of the above mechanism is based on the study relating to the infrared spectra of phenol or CYH adsorbed on the catalyst^{7),18)}. This study has made it clear that phenol adsorbs in the form of phenoxide, and CH interacts with the hydroxyl group on the surface of the catalyst. According to the above mechanism, phenol has a lone pair of electrons which tends to be attracted to the metal ion to form the above intermediate. In the case of catalysts whose activities increase with increase in electronegativity, this intermediate is unstable and readily forms a mixture of CHP isomers. The rate-determining step over these catalysts is regarded as I. On the other hand, in the case of catalysts whose activities decrease with increase in electronegativity, this intermediate is very stable. Since the benzene ring of phenol derivatives also interacts with the strong Brönsted sites, desorption of CHP is very difficult. The rate-determining step is regarded as III.

In this paper, we have considered the cause of volcano shape relation for alkylation of phenol



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with CYH to be the difference in the rate-determining step. Further studies are needed to define more specifically the reaction mechanism.

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