Meta Alkylation of Phenol on Alumina Catalysts

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The alkylation of phenol by C_1-C_3 alcohols as alkylating reagents was examined on alumina and alumina containing catalysts. Alumina showed a significant activity to *meta* position, especially in methylation and ethylation. For instance, the composition of *meta* isomer was 38% in cresols formed at 450°. Alumina–silica (1: 1) yielded 48% *meta* isomer. The latter catalyst was an acidic one, and the formation of *meta* isomer was in parallel with its acid strength.

To elucidate the mechanism of alkylation to *meta* position, the rearrangement of. phenylethers and the isomerization of *ortho* alkylphenols were investigated in the presence of phenol-[14]C. The ^{14}C-distribution in the product was then determined by the radio-gaschromatography and the ratio of intramolecular to intermolecular rearrangement was evaluated. The adsorbed state of phenol and alcohols at the reaction temperature was investigated with the infrared method, and the mechanism of alkylation was discussed therefrom.

Introduction

The catalytic alkylation of phenol to the aromatic nucleous with one step has been investigated by many workers. Ipatiew, Orlow and Petrow[2] obtained anisole and a small amount of *o*-cresol from phenol and methanol using aluminium hydroxide gel as a catalyst at 440°. The reaction was performed under 220 atm in a heterogeneous liquid phase. Cullinane and Chard[3] reported in their vapor phase reaction that 22.0% of *meta* isomer in cresol had been formed from methanol and phenol at 345° on alumina. Recently, Venuto, Hamilton, Landis and Wise,[4] who used zeolite as a catalyst, obtained 4% of *meta* isomer from ethanol and phenol at 220°.

The present authors have also investigated the alkylation of phenol with particular interest to the selective formation of *meta* isomer, and found that the selectivity is achieved on a condensed phosphoric acid-kieselguhr catalyst using C_2-C_4 olefins[5] and C_1-C_4 alcohols[6] as the alkylating reagents in the temperature range from 250 to 450°. For instance, using methanol as an alkylating reagent, *meta* isomer reached to 40% of cresols formed. In a later work, it was found that alumina-silica-magnesia has a high catalytic activity toward the methylation of phenol by methanol; the conversion reached to 80% of phenol and the products contained 50% *meta* isomer, with the composition of *o*-: *m*-: *p*-=3 : 5 : 2.

This report deals with the mechanism of the alkylation of phenol on γ-alumina, comparing with that on condensed phosphoric acid-kieselguhr. The alkylation of phenol is investigated in the presence of phenol-^{14}C, and the infrared spectroscopic observation of the active species adsorbed on γ-alumina is carried out at the reaction temperature.

Experimental

Alumina Catalyst——Alumina hydroxide gel (Fuji Chemicals Co., Ltd.), specific surface area of 116 m^2/g, was knead with water and pelleted to a cylindrical form of 2 mm × 3 mm. After being dried at 120° for 30 min, the pellets were calcined at 450° for 5 hours.

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1) Location: *3190 Gofuku, Toyama.*
2) W. Ipatiew, N. Orlow and A. Petrow, *Ber.*, **60B**, 130 (1927).
3) N.M. Cullinane and S.J. Chard, *J. Chem. Soc.*, **1945**, 821.
4) P.B. Venuto, L.A. Hamilton, P.S. Landis and J.J. Wise, *J. Catalysis*, **4**, 81 (1966).
5) M. Inoue, T. Nakagawa and S. Enomoto, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 1127 (1970).
6) M. Inoue and S. Enomoto, *SHOKUBAI (Catalyst)*, **10**, 106 (1968).

Alumina-Magnesia Catalyst——Aluminum hydroxide gel and magnesium hydroxide (Kishida Chemicals Co., Ltd.) were mixed and knead with water and prepared with the same way as the alumina catalyst.

Alumina-Silica Catalyst——Using aluminum hydroxide gel and silicic anhydride (Fuji Chemicals Co., Ltd.), specific surface area of 300 m^2/g, the catalyst was prepared with the same way as the alumina catalyst.

Phenol-^{14}C (U)——Supplied by The Radiochemical Centre, Amersham.

Gaschromatography——Phenol, *ortho, meta*, and *para* alkylphenols were separated and evaluated with the gaschromatograph, Yanaco G-800T: liquid phase, tricresyl phosphate (25%)+H_3PO_4 (3%); column, 3 mm×2 m; hydrogen flow rate, 20 ml/min; temperature, 120°; detector, TCD.

Radiogaschromatography——The radioactivity of phenol, *ortho, meta*, and *para* alkylphenol was recorded with Yanaco G-8 and Aloka RD-4. Experimental and analytical techniques have been reported earlier.

The IR Spectrum of Phenol and Methanol adsorbed on Alumina——γ-Alumina was dispersed with the supersonic wave of 400 kc for a few minutes, and spread and dried over a thin NaCl crystal plate, 0.5 mm in thickness. After connecting to the vacuum line, it was heated at 450° and evacuated to 10^{-2} mmHg. On the sample plate, phenol or methanol was adsorbed and recorded with Jasco IR-E.

Result and Discussion

The Alkylation of Phenol by Alcohols as the Alkylating Reagents

It has been known that some metal oxides show the ability of the alkylation of phenol to its *ortho* position selectively. For example, MgO,[7] CeO$_2$,[8] FeO[9] *etc.* produced *o*-cresol and 2,6-xylenol in the vapor phase heterogeneous system between 400 and 500°. No such an alkylating selectivity has been reported on γ-alumina even at 300°. The present authors found that, at 450°, not only *para* isomer but also *meta* isomer, which occupies 38.3% of cresol formed, is produced (Table I- No. 1). In the case of condensed phosphoric acid-kieselguhr, the alkylation to *meta* position was related with the number of acid site on the catalyst. So, it can be considered that the acid site on γ-alumina also plays an important role in both alkylation and isomerization. Our γ-alumina, prepared from alumina gel calcined at 500° for 3

TABLE I. Alkylation of Phenol with Alcohols on Alumina and Alumina containing Catalysts

No.	Catalysts	Alcohols[a]	Temp. (°C)	Conv. (%)	mono Alkylphenols			di-Alkyl-phenols (%)
					ortho (%)	meta (%)	para (%)	
1	Al_2O_3	methanol	450	61.3	41.2	82.8 38.3 78.0	20.5	17.2
2	Al_2O_3–SiO_2 (1:1)	methanol	450	78.4	34.1	47.8 85.7	18.1	0.4
3	Al_2O_3–MgO (1:1)	methanol	500	35.6	48.0	30.0 58.9	22.0	14.3
4	Al_2O_3–MgO (1:1)	ethanol	400	81.3	47.5	38.7 81.0	15.6	41.1
5	Al_2O_3–MgO (1:1)	*n*-propanol	350	57.2	50.0	29.2 100	20.8	0[b]
6	Al_2O_3–MgO (1:1)	isopropanol	350	7.1	50.0	28.6	24.0	0

a) mole ratio to phenol is 2.0   *b)* 19.0% of cracking products is observed.
carrier gas: N_2, 3l/hr feeding rate: 4 ml/hr

7) S.B. Hamilton, U.S. Patent. 3446856 (1968).
8) J.A. Sharp and R.E. Dean, Brit. Patent, 1124839 (1968).
9) W. Kunz, Brit. Patent, 717588 (1954).

hours, has in fact caused the Hammett indicator of $pK_a = +3.3$ to change its color to an acidic one in benzene.

It can be expected therefore that the composition of *meta* isomer in the methylated products is changeable depending on the acidic properties of the catalyst or by the addition of the second component. No. 2 and No. 3 of Table I show the results of such investigations. The alumina containing silica is often known as a "silica-alumina catalyst" whose acidity and acid strength are much greater than alumina or silica alone. Alumina-silica of equal weight ratio had the strongest acid site of $+1.2$ as indicated by the acid function, H_0, and gave rise to 50% *meta* isomer in the cresols formed. In contrast, when the catalyst containing magnesia, $H_0 = +4.8$, yielded 30.0% *meta* isomer at 500°. These results clearly indicate that the isomerization activity is parallel to the acid strength of the catalysts as far as the methylation concerns.

As to the conversion of phenol, the magnesia added catalyst brought forth a higher yield in ethylation and propylation than alumina or magnesia alone (No. 4). Then it may be considered that these catalysts have a bifunctional property for alkylation and isomerization. This point will also be discussed in the subsequent section. However the alumina and alumina containing catalyst showed a low activity and narrow temperature range (300 to 350°) to propylation (No. 5, 6). Since somewhat higher conversion was obtained with propylation on condensed phosphoric acid-kieselguhr, and moreover, the distribution of cresol isomers produced appeared to be different with each other catalyst, there seem to be some differences in the reaction mechanism between the two catalyst systems.

The Rearrangement of Anisole and the Isomerization of o-Cresol in the Presence of Phenol-^{14}C

On a condensed phosphoric acid-kieselguhr catalyst, cresols were produced from anisole through the rearrangement and the isomerization.[10] *m*-Cresol was aslo produced on γ-alumina as shown in Table II.

TABLE II.   Rearrangement of Methyl Group in Presence
of Labeled Phenol on Alumina at 450°

No.	Compounds[a]	Phenol (%)	mono Alkylphenols			Xylenols (%)
			ortho (%)	meta (%)	para (%)	
1	anisole	61.1	57.0	36.1 30.9	12.1	2.8
	(A/B %)[b]	(65)	(49)	(56)	(45)	—[c]
2	*ortho* cresol	65.2	52.3	34.8 35.4	12.3	0
	(A/B %)	(58)	(57)	(48)	(52)	—[c]

a) mixed with the same weight of phenol-^{14}C
b) A: specific radio activity of products   B: specific radio activity of initial phenol-^{14}C (4 μci/ml)
c) Counts were so small to calculate.

Magnesia showed very poor ability to the rearrangement of anisole at 500°, but in methylation the conversion to o-cresol was 70% in the equimolecular reaction between phenol and methanol at 500° (Table III). These results may suggest that a direct alkylation to *ortho* position of phenol occurs without passing through anisole. Moreover, on magnesia, the isomerization to *meta* or *para* position did not take place.[7] The inactivity would probably be due to the fact that the catalyst is basic in character.

This kind of reaction may be favorable on alumina because of its amphoteric character. So, the mechanism was further investigated with the radiogaschromatography using phenol-^{14}C

10) M. Inoue and S. Enomoto, *Chem. Pharm. Bull.* (Tokyo), **19**, 2518 (1971).

TABLE III.   Alkylation of Phenol with Methanol and Rearrangement
of Anisole on Magnesia

No.	Reactants	Temp. (°C)	Anisole (%)	Phenol (%)	o-Cresol (%)	2,6-Xylenol (%)	2,4-Xylenol (%)
1	phenol methanol[a]	400	trace	89.9	10.1	0	0
2	phenol methanol[a]	500	trace	33.8	47.6	15.2	2.4
3	anisole	400	98.7	1.3	0	0	0
4	anisole	500	86.6	12.3	1.1	0	0

a) mole ratio to phenol is 1.0   carrier gas: N_2, 3 l/hr   feeding rate: 4 ml/hr

as a tracer.   It was presumed that γ-alumina is a bifunctional catalyst, both rearrangement of anisole and isomerization of o-cresol take place on its acid site, the alkylation occuring consecutively as it did on the condensed phosphoric acid-kieselguhr catalyst (Type I).   Assuming that the Type I reaction is the main course, the rearrangement of anisole in the co-existence of phenol-^{14}C is expected to produce an equal amount of radioactive and nonradioactive cresols.   In other words, the migration of the methyl group should have an equal probability between intra- and intermolecular reaction.

On the other hand, when the methylation to the ortho position of phenol takes place without passing through phenylether, as was seen on magnesia (Type II), the exchange of methyl group may be observed.

The rearrangement of anisole at 300 and 450° in the presence of phenol-^{14}C is shown in Fig. 1 and 2, respectively.   At 300°, o-cresol is main product and the specific radioactivity reaches to a half value of the initial phenol-[14]C.   This relation is also kept in m- and p-cresol after the isomerization at 450°.   Moreover, the presence of the radioactive species in unrearranged anisole indicates the migration of methyl group from anisole to labeled phenol.   These behaviours suggest that the reaction proceeds with Type I.
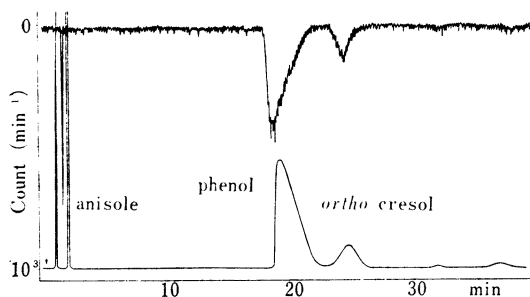

Fig. 1.   Radiogaschromatogram in Rearrangement of Anisole in Presence of labeled Phenol on Alumina at 300°
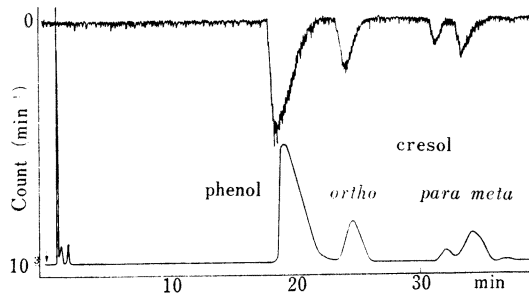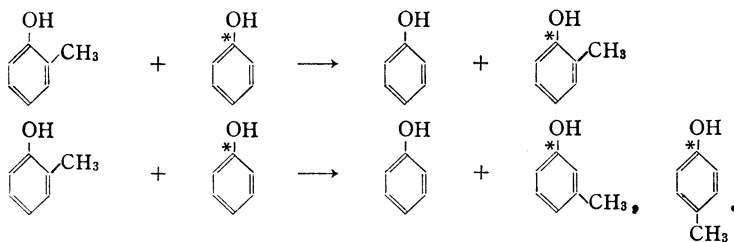

Fig. 2.   Radiogaschromatogram in Rearrangement of Anisole in Presence of labeled Phenol on Alumina at 450°

In contrast, an proof of another route to m- and p-cresol is presented in Table II- No. 2. The isomerization of o-cresol in the presence of phenol-^{14}C gives labeled m- and p-cresol. So, it is considered that either one or both steps are intermolecular reaction;

Now, the isomerization of *o*-cresol takes intramolecular mechanism as already seen on condensed phosphoric acid-kieselguhr.   So, the methyl group attached to the *ortho* position of phenol is exchanged on basic site prior to the isomerization.

The reaction intermediates of Type II is, therefore, considered to be methyl cation adsorbed on the basic site of alumina.
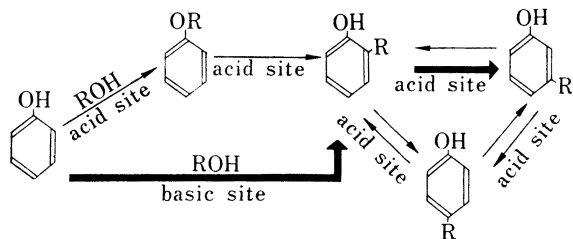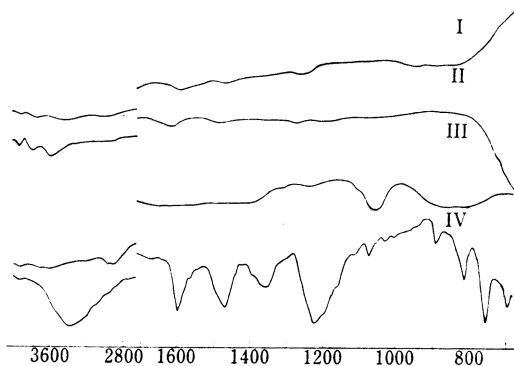

Chart 1

Fig. 3.   The Infrared Spectra of Phenol and Methanol chemisorbed on Alumina and Magnesia

I: phenol on alumina at 450°
II: phenol on magnesia at 400°
III: methanol on alumina at 420°
IV: phenol vapor at 200°

IR Spectra of Phenol and Methanol adsorbed on γ-Alumina

The state of phenol adsorbed on γ-alumina at 450° was first examined by infrared (IR).   As shown in Fig. 3, although the spectrum was weak, the hydroxyl gruop of phenol at 3200 cm^{-1} was detectable.   The spectrum became weak with rising temperature and disappeared at 450°.   The spectra at 1300 cm^{-1} and 1600 cm^{-1} were considered to originate also from adsorbed phenol.   Especially the band at 1250 cm^{-1} was in accord with the C-O band of aluminium phenolate.[11]

The same spectrum was recognized also on magnesia; the band at 1270 cm^{-1} was attributed to that of magnesium phenolate.   From the above results, it became obvious that phenol adsorbs tightly on the metal oxides.

The IR spectrum of adsorbed methanol was then investigated.   The spectra were observed in this case at 1070 cm^{-1}, 1220 cm^{-1}, 1400 cm^{-1}, and 2900 cm^{-1} respectively.   All of them were ascribed to adsorbed methanol, suggesting that the adsorption of methanol on γ-alumina is also strong.   Consequently, the IR studies for adsorbed phenol and methanol led us to conclude that the alkylation proceeds through the bimolecular condensation of the two reactants on the surface.

The alkylation of phenol by alcohols seems to proceed on γ-alumina according to the two paths as shown in Chart 1.   The adsorbed phenol is alkylated by alcohols on the acid site to form anisole.   Anisole then rearranges to give, for example, *o*-cresol.   The rearrangements take place on the acid site.

The other pathway is related with the basic site, the tightly held phenol introduces the direct alkylation to ortho position.   It is not clear yet that to what extent the two pathways contribute to the formation of final products.   The presence of basic site on alumina has generally been accepted, and in a certain instance the basic site are reported to be more abundant than the acid site.[12]   From the observation that phenol has been alkylated to its *ortho*

11) T. Shimanouchi, "Analysis of Infrared Spectra," Nankodo, Tokyo, 1960, P78.
12) G.M. Schwab and H. Kral, 3rd. Internl. Congr. Catalysis (Amsterdam).

position with higher conversion than the methylation on condensed phosphoric acid-kieselguhr, this type of reaction is considered to be predominant.

Furthermore, alumina catalysts have shown a very poor activity similar to magnesia catalysts in the propylation of phenol, suggesting that the basic site also participate in the reactions. Thus, it is suggested that the alkylation of phenol to its *ortho* position may proceeds on the basic site without passing through anisole. On the other hand, the isomerization of *ortho* form to yield *meta* or *para* form may take place in the acid site.