A Study of Catalysis by Metal Phosphates. IV.[1] The Alkylation of Phenol with Methanol over Metal Phosphate Catalysts

Fumio Nozaki and Isao Kimura

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 280

(Received August 26, 1976)

The catalytic methylation in the vapor phase over various metal phosphates has been investigated using a conventional flow reactor at temperatures ranging from 350 to 500 °C under atmospheric pressure. The $Ca_3(PO_4)_2$ catalyst was excellent in both its activity and its selectivity for ortho-methylation, giving predominantly *o*-cresol and 2,6-xylenol, whereas the BPO_4 or $CaHPO_4$ catalyst simultaneously promoted the formation of anisole. The activity of $Ca_3(PO_4)_2$ was significantly higher than that of the CaO or MgO catalyst. The influences of the reaction temperature, the contact time, and the calcination temperature of the catalyst upon the conversion of phenol, and the yields of the products were investigated in detail over the $Ca_3(PO_4)_2$ catalyst. The activities and the selectivities of various catalysts were discussed in connection with their acid-base properties. The mechanism of the participation of both the acidic and basic sites in the methylation was also discussed.

The alkylation of phenol in the ortho position has been of interest in recent years,[2] and the catalytic process using methanol as an alkylating reagent has been investigated by several workers.[3-7] The alkylation reactions of phenol or cresol using C_2—C_4 olefins or C_1—C_4 alcohols have also been studied over various catalysts.[8-10] However, no study of the phosphate catalyst has been reported.

Our preliminary study has revealed that calcium orthophosphate has a significant activity and an interesting selectivity for the alkylation of phenol with methanol in the vapor phase. The present paper will describe the behavior of metal phosphates as a catalyst. The correlation between the selectivity for the reaction and the acid-base character of the catalysts will also be discussed.

Experimental

Catalysts. The metal phosphate catalysts were obtained from guaranteed commercial reagents by the usual method of pellet-catalyst preparation, which involves wet mixing and extruding in order to mold the catalyst. All the catalysts were in the form of 1—2 mm pellets. The CaO and MgO catalysts used to characterize the phosphate catalysts were prepared by the thermal decomposition of the $Ca(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2$ reagents respectively. Unless otherwise noted, the catalysts were activated before use by calcining at 500 °C for 3 h in a stream of air.

Apparatus and Procedure. A usual type of flow reactor consisting of a 18 mmϕ glass tube was used to perform the catalytic tests. Unless otherwise specified, the reactor contained 2 g of the catalyst. The reactor was vertically supported and externally heated in an electric furnace. The upper part of the reactor was packed with small glass beads, thereby vaporizing and preheating the reactants. A stream of nitrogen was passed through the catalyst bed at 500 °C for 1 h and then the temperature was lowered to the reaction temperature in a stream of nitrogen. A methanol–phenol mixture of a known composition was fed into the reactor at a constant rate by means of a microfeeder, and then carried by nitrogen to the catalyst bed. The outlet vapor was condensed in a trap cooled with an ice bath, and samples for analysis were collected periodically. The condensed liquid products were analyzed by means of a gas-chromatographic unit containing a 3-m column of Silicone DC-550. The column was operated at 150 °C, with hydrogen as the carrier gas. The products were identified by a comparison of their chromatograms with those of authentic samples. Besides the methylation of phenol, methanol was simultaneously consumed by the gasification which was a side-reaction, giving such non-condensable products as CO, CO_2, and CH_4. However, no detailed measurement of the non-condensable products has been made because they were formed to only a small extent throughout the catalytic tests in which the phosphates were used as catalysts. The conversion of phenol and the yields of the products were expressed in mol%. The liquid products obtained consisted mainly of *o*-cresol, 2,6-xylenol, anisole, 2,4,6-trimethylphenol, 2,4-xylenol, and small amounts of *m*, *p*-cresol. Very small peaks of unknown products were detected in the gas-chromatograms, but their formation was neglected in the calculation of the conversion and the selectivity. The selectivity for the ortho-methylation, S_o, was defined as follows:

$$S_o = \frac{\text{yield of } (o\text{-cresol} + 2,6\text{-xylenol})}{\text{total conversion of phenol, } x}$$

The selectivity for anisole formation, S_A, and the selectivity to the other products (*m*- and *p*-cresol+2,4-xylenol+2,4,6-trimethylphenol), S_B, were defined as follows:

$$S_A = \frac{\text{yield of anisole}}{\text{total conversion of phenol, } x}$$

$$S_B = 1 - (S_o + S_A)$$

As an indication of the contact time in the flow reactor, we used W/F, defined as follows:

$$W/F = \frac{\text{catalyst weight (g)}}{\text{feed rate of the sum of reactants and nitrogen (mol/h)}}$$

The powdered catalyst samples calcined at 500 °C for 3 h in air were used for the measurements of their acidity and basicity. The acidities of the catalysts were measured by usual *n*-butylamine titration, using the Hammett indicators. According to the method of Tanabe *et al.*,[11] the basicities of the catalysts were measured by titrating them with a benzoic acid–benzene solution, using bromothymol blue ($pK_a = 7.1$) and phenolphthalein ($pK_a = 9.3$) as indicators.

Results and Discussion

Catalyst Activity and Change in Activity with the Process Time. The changes in the activity and selectivity during the course of the reaction were generally not serious, although the degree of the change depended on the species of the catalysts. Henceforth, in order to

Table 1. Activities and selectivities of various catalysts

Conditions: reaction temperature (t)=460 °C, W/F=14.5 g h/mol, feed molar ratio (m) of methanol/phenol/N_2=2.0/1.0/1.2.

Catalyst		$Ca_3(PO_4)_2$	$CaHPO_4$	$Ca(H_2PO_4)_2$	BPO_4	CaO	MgO
Conversion of phenol, x (%)		77.7	26.4	1.0	47.0	7.6	48.0
Selectivity, S_o (%)		88	28	0	46	75	80
Yield (%)	anisole	0.6	19.0	1.0	25.4	0.6	1.9
	o-cresol	38.2	7.4	0	17.8	5.7	30.5
	m,p-cresol	0	0	0	0	1.3	4.8
	2,6-xylenol	30.3	0	0	3.8	0	7.9
	2,4-xylenol	3.1	0	0	0	0	1.8
	2,4,6-trimethylphenol	5.5	0	0	0	0	1.1
Conversion of methanol, x_M (%)		42.1	—	—	95.8	4.6	—
Selectivity for methylation, S_M (%)		93	—	—	25	83	—

compare the catalysts, we will use the activity data obtained around 1.5 h after the start of the reaction. The activities and the selectivities of various catalysts are shown in Table 1. It can be seen from Table 1 that the $Ca_3(PO_4)_2$ catalyst is excellent in activity and selectivity for ortho-methylation, leading to *o*-cresol and 2,6-xylenol. Another characteristic of the $Ca_3(PO_4)_2$ catalyst is the fact that it is liable to form highly methylated products, such as xylenol isomers and 2,4,6-trimethylphenol. The ortho-selectivity of the BPO_4 catalyst is far less than that of the $Ca_3(PO_4)_2$, since the BPO_4 gives rise to anisole in a large quantity even though it has a substantial activity. Both the $CaHPO_4$ and $Ca(H_2PO_4)_2$ are somewhat inferior to the other catalysts. The CaO and MgO catalysts have a low activity, though it is high in ortho-selectivity. Tanabe *et al.*[4,5] have already pointed out that the CaO or MgO catalyst has a high selectivity for ortho-methylation. In agreement with their papers, our experiment has also revealed that the CaO and MgO catalysts have a high selectivity, although their activities are far less than that of the $Ca_3(PO_4)_2$. In the cases of the other phosphate catalysts, the catalytic tests gave the following results; $Ni_3(PO_4)_2$: x=8%, S_O=38%, S_A=62%, $AlPO_4$: 9, 56, 44%, $CrPO_4$: 19, 21, 79% and $Zr_3(PO_4)_4$: 6, 33, 67%, respectively. The activities and the ortho-selectivities of these phosphate catalysts were appreciably inferior to those of the $Ca_3(PO_4)_2$; an additional characteristic of their behaviors as catalysts was the fact that scarcely any formation of *m,p*-cresol, 2,4-xylenol, or 2,4,6-trimethylphenol was found. As has been described in previous papers,[1,12] $Cd_3(PO_4)_2$ is an effective catalyst for the dehydrogenation of alcohols, by analogy with the $Ca_3(PO_4)_2$ catalyst. However, $Cd_3(PO_4)_2$ exhibited very little activity for the methylation of phenol. This seems to be the reason for the low thermostability of the $Cd_3(PO_4)_2$ catalyst.[12]

During the course of the methylation, the phenol is not entirely decomposed to form benzene or gaseous compounds. In contrast, methanol is consumed through two simultaneous reactions, the methylation of phenol and the gasification giving such non-condensable products as CO, CO_2, and CH_4. The effectiveness of the catalyst should be discussed not only in terms of the conversion of phenol, but also in terms of the fraction of methanol utilized as an alkylating reagent. An important characteristic of the $Ca_3(PO_4)_2$ catalyst to be noted here is that only a small % of the methanol converted is consumed for gasification. It must be generally accepted that the MO–Fe_2O_3 catalyst developed by Kotanigawa *et al.*[3] is more active than the $Ca_3(PO_4)_2$ catalyst. The MO–Fe_2O_3 catalyst, however, leads to significant amounts of gasification of methanol; hence, it can be said that the $Ca_3(PO_4)_2$ catalyst is more effective in the selectivity of methanol than the MO–Fe_2O_3 catalyst.

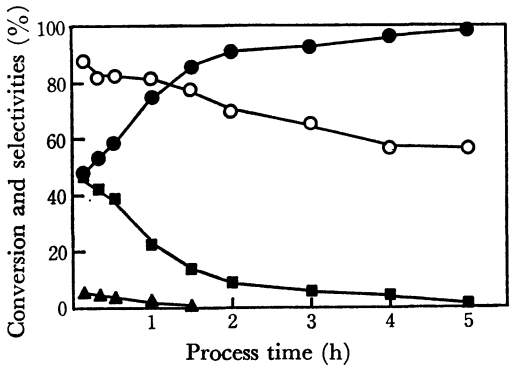


Fig. 1. Changes in activity and selectivity of $Ca_3(PO_4)_2$ catalyst with process time.
Conditions: t=460 °C, W/F=14.5 g h/mol, m=2.0/1.0/1.2.
○: Conversion of phenol (x), ●: selectivity for ortho-methylation (S_O), ▲: selectivity for anisole formation (S_A), ■: selectivity to the other products (S_B).

The change in the activity and selectivity of the $Ca_3(PO_4)_2$ catalyst with the process time are illustrated in Fig. 1. Both the activity and the selectivity change rapidly at the initial period, and then they gradually approach almost constant values. The selectivity for ortho-methylation, S_O, increases with the process time and approaches 100% after the reaction had been continued for 4 h. In contrast, the selectivity to the other products, S_B, decreases rapidly and is lowered to a very small value with an increase in the process time. The selectivity for anisole formation, S_A, is allowed to continue at a small value and then becomes practically negligible around 2 h after the start of the reaction. Consequently, only two products, *o*-cresol and 2,6-xylenol, are obtained after the reaction has been continued for 5 h or more. Such a decrease in activity

and change in selectivity as are shown in Fig. 1 might be due to the disappearance of active sites, leading to the formation of a highly methylated product or anisole by the deposition of a carboneous substance. After the reaction has been continued for several hours, however, the catalyst surface is brought into a situation favorable to ortho-methylation and the subsequent catalytic reaction reaches an almost steady state.

Effects of the Reaction Temperature and Contact Time. The effect of the reaction temperature on the conversion, the selectivity, and the yields of the products was investigated with the $Ca_3(PO_4)_2$ catalyst. The results are shown in Figs. 2 and 3; the data were obtained by using a fresh catalyst in each run and by analyzing the samples collected 1.5 h after the start of the reaction. The higher the reaction temperature, the higher the conversion and the yield of *o*-cresol, 2,6-xylenol, or 2,4,6-trimethylphenol became. The selectivity for ortho-methylation was approximately 80%, regardless of the reaction temperature. The temperature providing the maximal yields of anisole and 2,4-xylenol were about 400 and 430 °C respectively. However, their yields did not exceed 5%.

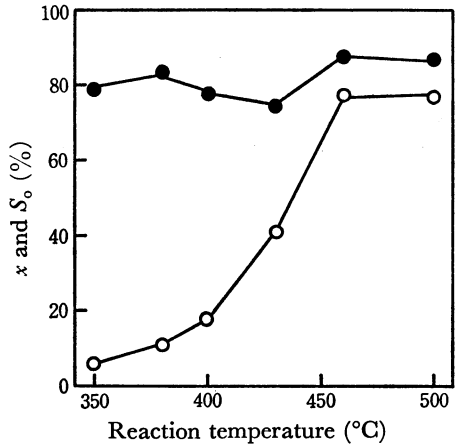


Fig. 2. Effect of reaction temperature on conversion and selectivity.
Conditions: $Ca_3(PO_4)_2$ catalyst, W/F=14.5 g h/mol, m=2.0/1.0/1.2.
○: Conversion of phenol (x), ●: selectivity for ortho-methylation (S_o).

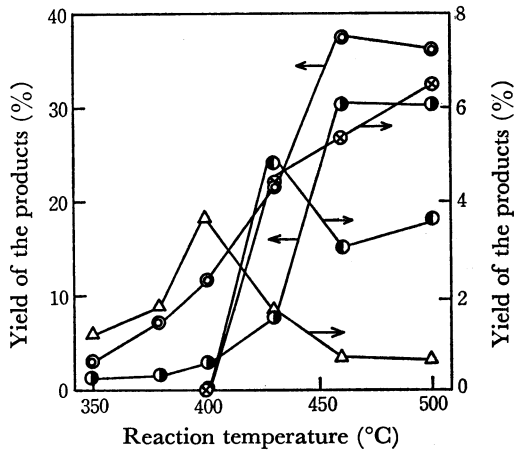


Fig. 3. Correlation between reaction temperature and yield of the products.
Conditions are the same as for Fig. 3.
◎: *o*-Cresol, ◑: 2,6-xylenol, ◐: 2,4-xylenol, ⊗: 2,4,6-trimethylphenol, △: anisole.

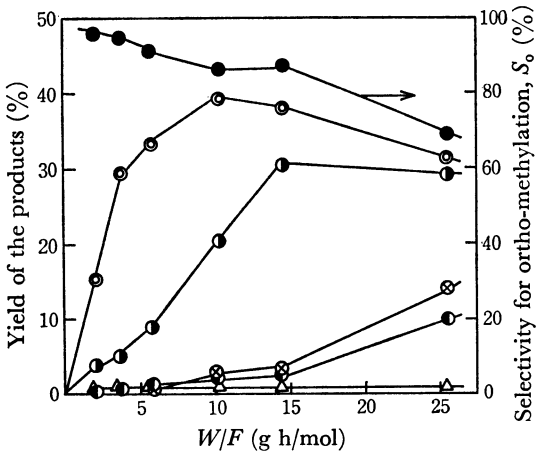


Fig. 4. Yield and selectivity over $Ca_3(PO_4)_2$ catalyst as a function of W/F.
Conditions: t=460 °C, m=2.0/1.0/1.2.
Symbols are the same as those defined in Figs. 2 and 3.

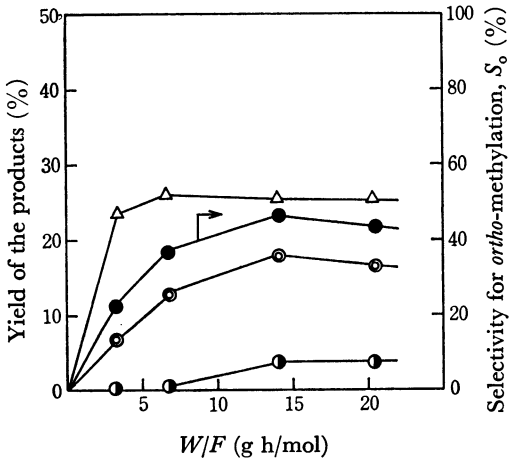


Fig. 5. Yield and selectivity over BPO_4 catalyst as a function of W/F.
Conditions and symbols are the same as for Fig. 4.

The effects of W/F on the yields of the products are shown in Figs. 4 and 5. Figure 4 indicates that the $Ca_3(PO_4)_2$ catalyst gives, selectively, *o*-cresol and 2,6-xylenol in the low range of W/F. With an increase in W/F, the consecutive methylation of *o*-cresol to xylenols and trimethylphenol is gradually increased, but the formation of anisole is slight over the entire range of W/F. Figure 5 indicates that, in the case of the BPO_4 catalyst, the increase in W/F does not result in a remarkable increase in the yields of the products or in the selectivity for ortho-methylation. Anisole is predominantly formed over the whole range of W/F, but no definitive maximum in the yield of anisole is perceived throughout the experimental range of W/F. The yields of xylenol isomers were vanishingly small, and such highly methylated products as trimethylphenol were completely missing, even at the highest range of W/F.

TABLE 2. ACID-BASE PROPERTIES OF VARIOUS CATALYSTS

Catalyst	Acidity (mmol/g)			Basicity (mmol/g)
	$H_0 \leqq 3.3$	$H_0 \leqq 4.8$	$H_0 \leqq 6.8$	$H_0 \geqq 7.1$
$Ca_3(PO_4)_2$	0	0	0.132	0.053
$CaHPO_4$	0	0.046	0.073	0
$Ca(H_2PO_4)_2$	0.196	—[b]	—[a]	0
BPO_4	0.220	—[b]	0.370	0
CaO	0	0	0.043	0.066

a) The acidity ($H_0 \leqq 6.8$) of $Ca(H_2PO_4)_2$ could not be measured quantitatively because of the formation of a precipitate. b) The measurements were not carried out.

Acid-Base Property of the Catalyst and the Catalytic Activity. The acid-base properties of the catalysts are shown in Table 2. The strong basic site with $H_0 \geqq 9.3$ was not found in any catalyst. Between the catalytic activities and the acid-base properties of the catalysts, no simple correlation can be observed by comparing Table 1 with Table 2. Excluding the case of the $Ca(H_2PO_4)_2$ catalyst, however, it is likely that anisole is produced over the BPO_4 or $CaHPO_4$ catalyst with acidic sites ($H_0 \leqq 4.8$) but no basic sites, and that the ortho-methylation can occur over the catalysts with both weak acidic sites ($H_0 \leqq 6.8$) and basic sites.

In order to make this aspect clearer, we have investigated the relationship between the catalytic activity and the acid-base property, using a series of $Ca_3(PO_4)_2$ catalysts calcined at various temperatures. The results are shown in Figs. 6 and 7. Both the acidic strength and the basic strength of the $Ca_3(PO_4)_2$ catalyst remained unaltered by a change in the calcination temperature, although either the acidity ($H_0 \leqq 6.8$) or the basicity ($H_0 \geqq 7.1$) varied, as is shown in Fig. 6. Figure 6 indicates that the acidity decreases monotonously with the rise in the calcination temperature, while the basicity has its maximum at the calcination temperature near 550 °C. Figure 7 indicates that the catalyst activity (the conversion of phenol) slightly increases with rise in the calcination temperature from 460 to 500 °C, passes

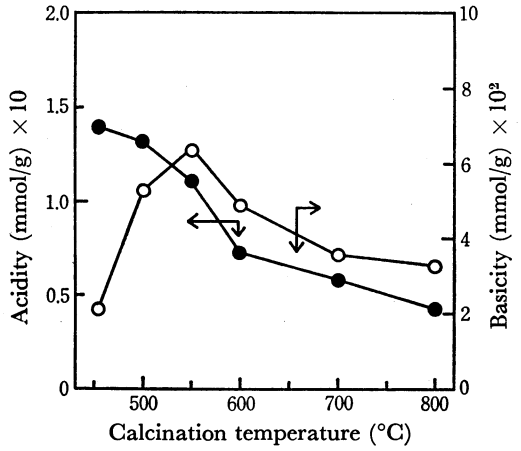


Fig. 6. Acidity and basicity of $Ca_3(PO_4)_2$ calcined at various temperatures.
●: Acidity (measured at $H_0=6.8$), ○: basicity (measured at $H_0=7.1$).

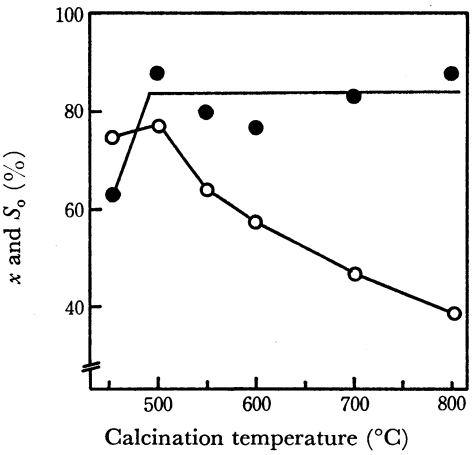


Fig. 7. Activity and selectivity of $Ca_3(PO_4)_2$ catalyst calcined at various temperatures.
Conditions and symbols are the same as for Fig. 2.

through a maximum at about 500 °C, and then significantly decreases. In contrast, the selectivity for ortho-methylation remains almost constant at temperatures ranging from 500 to 800 °C, except for the low selectivity of the catalyst prepared at 460 °C. A comparison of Fig. 6 with Fig. 7 suggests that the catalytic activity may be correlated to both the acidity and basicity, whereas the ortho-selectivity essentially depends on whether or not the basic sites coexist with acidic sites.

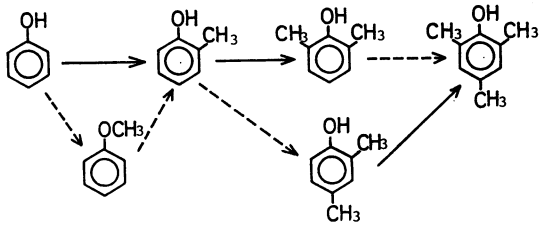
Reaction Pathway and Reaction Mechanism. By considering the fact that a maximal yield in the anisole formation is not observed in Fig. 4, the ortho-methylation giving *o*-cresol and 2,6-xylenol is expected to occur through a direct methylation of phenol, not through the formation of phenylethers, such as anisole or *o*-methylanisole, and their subsequent isomerization. In order to make more clear the reaction pathway of methylation, we have carried out additional catalytic tests between anisole, *o*-cresol or xylenols, and methanol. The results are summarized in Table 3. When anisole alone was passed through the $Ca_3(PO_4)_2$ catalyst under

TABLE 3. CATALYTIC REACTIONS BETWEEN ANISOLE, *o*-CRESOL, 2,4-XYLENOL, OR 2,6-XYLENOL AND METHANOL OVER THE $Ca_3(PO_4)_2$ CATALYST
The conditions are the same as in Table 1, except for the methanol/reactant feed ratio.[a]

Reaction[a]	Anisole–methanol	*o*-Cresol–methanol	2,6-Xylenol–methanol	2,4-Xylenol–methanol
Conversion[b] (%)	48	40	25	66
	Yield of the product (%)			
Phenol	2	3	0	0
o-Methylanisole	6	3	0	0
o-Cresol	8	—	8	4
m,p-Cresol	0	0	0	1
2,6-Xylenol	16	23	—	0
2,4-Xylenol	5	7	0	—
2,4,6-Trimethylphenol	11	4	17	61

a) Feed molar ratio of methanol/anisole, methanol/*o*-cresol, *etc.*=1. b) Conversion of anisole, *o*-cresol, *etc.*

the same conditions as those described in Table 3, the anisole was rearranged, giving a small amount of *o*-cresol (in a 7.5% yield); it was partly demethylated to give phenol (in a 9.8% yield). From a comparison of Table 3 with the results shown in the other tables and figures, the following speculations are possible with respect to the reaction pathway of methylation: (1) the formation of *o*-cresol is due mostly to the direct methylation of phenol; (2) anisole is scarcely methylated at all to form *o*-methylanisole; (3) the isomerization of *o*-cresol to anisole or *m,p*-cresol is not observed; (4) xylenol isomers are formed by a consecutive methylation of *o*-cresol, whereupon it tends to form 2,6-xylenol rather than 2,4-xylenol, and (5) 2,4,6-trimethylphenol is formed by the further methylation of xylenol isomers, whereupon 2,4-xylenol is more readily methylated than 2,6-xylenol. Thus, the reaction pathway of methylation over the $Ca_3(PO_4)_2$ catalyst may be depicted as the following steps:



where the(→)arrow shows the main route of the methylation and(⇢), the sub-route. The behavior of $Ca_3(PO_4)_2$ as a catalyst was characterized by a selective formation of the ortho alkylated products. The reaction pathway described above is intrinsically consistent with the result obtained over the basic catalysts by Tanabe *et al.*[4] and by Enomoto *et al.*[7] Tanabe[13] and Enomoto *et al.*[7] have already pointed out that acidic catalysts, such as SiO_2–Al_2O_3 or condensed phosphoric acid, promote the reactions, giving phenylethers or *m*-alkylated products, while basic catalyst, such as MgO or ZnO–Fe_2O_3, promote the direct alkylation, giving the *o*-methylphenols without passing through phenylethers as an intermediate. According to their argument, the $Ca_3(PO_4)_2$ catalyst appears to be characteristically basic. This is not in conflict with our previous reports,[1,12] in which the $Ca_3(PO_4)_2$ has been characterized as a basic catalyst for the dehydrogenation of alcohols. However, it should be noted that the ortho-methylation of phenol depends not only on the basic sites, but also on the acidic sites, as has been mentioned above.

The acid-base properties of the colored phosphates, such as $Ni_3(PO_4)_2$ or $CrPO_4$, are difficult to measure by the titration method using Hammett indicators. Thus, instead of using the experimentally found values of the acid-base properties of the catalysts, the electronegativities (x_i) of the metal ions[14] in the phosphate or oxide catalysts were used as an indication of the acidic or basic strength, according to the theory proposed by Tanaka.[14] The selectivities for the ortho-methylation of various catalysts are shown in Fig. 8 as functions of the parameter, x_i. Figure 8 shows that the correlation between S_o and x_i has a rough tendency to move towards a low selectivities with the increase in x_i. This

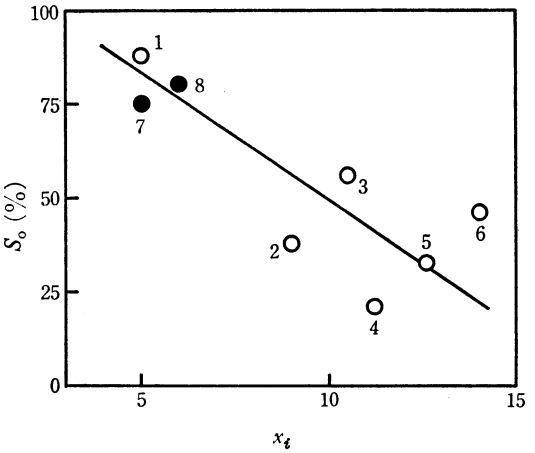


Fig. 8. Correlation between S_o and x_i.
Catalyst—1: $Ca_3(PO_4)_2$, 2: $Ni_3(PO_4)_2$, 3: $AlPO_4$, 4: $CrPO_4$, 5: $Zr_3(PO_4)_4$, 6: BPO_4, 7: CaO, 8: MgO.

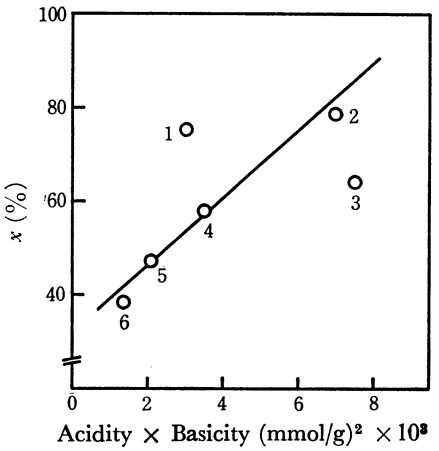


Fig. 9. Correlation between acid-base property and catalytic activity of $Ca_3(PO_4)_2$ calcined at various temperatures.
Calcination temperature—1: 460, 2: 500, 3: 550, 4: 600, 5: 700, 6: 800 °C.

downward trend in the selectivity on x_i is intrinsically the same result as those reported by Tanabe *et al.*[10,13] On the other hand, the change in the activity depending on the variety of catalyst was too complicated to deal with quantitatively. In the limited case of the $Ca_3(PO_4)_2$ catalyst calcined at various temperatures, however, there was a rough correlation between the acid-base property (Fig. 6) and the catalyst activity (the conversion of phenol in Fig. 7), as is shown in Fig. 9. The upward trend in the activity with an increase in the term of (acidity)·(basicity) presumably suggests that the catalytic methylation is attributable to the mechanism involving both the acidic and basic sites. Further details of the reaction scheme and the catalyst structure must remain the subjects of future study.

References

1) Part III of this series: F. Nozaki and Y. Iimori, *Bull. Chem. Soc. Jpn.*, **49**, 567 (1976).
2) A. Tasaka, *Shokubai*, **15**, 155 (1973).
3) T. Kotanigawa, M. Yamamoto, K. Shimokawa, and Y.

Yoshida, *Bull. Chem. Soc. Jpn.*, **44**, 1961 (1971).

4) T. Nishizaki and K. Tanabe, *Shokubai*, **14**, No. 4 (Abstract of the 31st Annual Meeting of Catalysis Society of Japan), p. 138 (1972); *ibid.*, **15**, No. 4 (Abstract of the 33 rd Annual Meeting of Catalysis Society of Japan), p. 94 (1973).

5) H. Hattori, K. Shimazu, N. Yoshii, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **49**, 969 (1976).

6) N. Takamiya, Y. Nakamura, M. Uomori, and S. Murai, *Nippon Kagaku Kaishi*, **1974**, 1852.

7) M. Inoue and S. Enomoto, *Chem. Pharm. Bull.*, **19**, 2518 (1971); *Shokubai*, **15**, No. 4 (Abstract of the 33 rd Annual Meeting of Catalysis Society of Japan), p. 98 (1973).

8) Y. Ogata and M. Itoh, *Kogyo Kagaku Zasshi*, **70**, 911 (1967).

9) M. Nitta, K. Aomura, and K. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 2360, 2897 (1974).

10) T. Yamanaka and K. Tanabe, *Shokubai*, **17**, No. 4 (Abstract of the 37 th Annual Meeting of Catalysis Society of Japan), p. 102 (1975).

11) T. Takeshita and K. Tanabe, *Shokubai*, **7**, 467 (1965).

12) F. Nozaki and H. Ohta, *Bull. Chem. Soc. Jpn.*, **47**, 1307 (1974).

13) K. Tanabe, *Shokubai*, **17**, 72 (1975).

14) K. Tanaka, "Shokubai Kogaku Koza," Vol. 10, ed by the Catalysis Society of Japan, Chijin Shokan, Tokyo (1967), p. 752.