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The Methylation of Phenol and the Decomposition of Methanol on ZnO-Fe_2O_3 Catalyst

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As a result of a series of studies, ZnO-Fe_2O_3 catalysts have been shown to promote the selective methylation (k_1) of phenol at the ortho position and also to promote the decomposition of methanol (k_2). The activation energies were determined to be 22 ± 2 kcal/mol for the methylation and 27 ± 3 kcal/mol for the decomposition. The selectivity factor ($S=k_1/k_2$) of the simultaneous reaction was determined for five types of catalysts in order to estimate the most favorable catalyst for the methylation. The selectivity factor of these catalysts decrease with the rise in the calcination temperature. For example, the S on the catalysts calcined at 500 °C is approximately at unity but the S on the catalysts calcined at 800 °C is at about 0.4. These results suggest that the calcination using the present catalysts should be controlled at a low temperature.

In the vapor-phase reaction on a solid catalyst, the selectivity for a desired product is said to be enormously affected by the pore structure of the catalyst.[1,2] However, there have been few experimental studies treating the effects of the pore structure on the selectivity for a desired reaction. Weisz *et al.*, however, reported the effects of pore sizes in the cracking of cyclohexane on a chromia-alumina catalyst.[3] Further, they reported the relations between the pore sizes and the selectivity for the dehydration of *iso*-butyl alcohol and *n*-butyl alcohol on a calcium aluminosilicate.[4]

The present author previously demonstrated that ZnO–Fe_2O_3 catalysts promoted the selective methylation of phenol at the ortho position and that it simultaneously promoted the decomposition of methanol.[5] Further, the relations between the preparative methods and the pore structures of the ZnO–Fe_2O_3 catalysts were studied.[6] In this paper, the present author will, therefore, discuss the relations between the preparative methods of the ZnO–Fe_2O_3 and the selectivity of the methylation of phenol to the decomposition of methanol on five types of ZnO–Fe_2O_3 catalysts.

Experimental

Apparatus and Reaction Conditions. A conventional flow-type reaction apparatus (reactor : Pyrex glass, 18 mm, i.d.) was used. A mixture of 1 mol of phenol and 5 mol of methanol was introduced into the vaporizer. The reaction vapors were carried with nitrogen gas onto the catalyst bed. The partial pressures of the phenol, methanol, and nitrogen gas in the reaction system were 0.105 atm, 0.515 atm, and 0.38 atm respectively. The time factor, W/F, was changed from 6 to 36 g-cat.h/mol-feed, and the reaction temperature was selected between 300 °C and 400 °C.

Analysis of the Reaction Products. The contents of the reaction products were quantitatively analyzed by means of gas chromatography. In the packed columns for gas chromatography, silicon oil DC 550 was used for analyzing aromatics, porapak Q was used for analyzing water and methanol in liquid products, and active charcoal was used for analyzing gaseous products.

Catalysts. The catalysts were prepared by the procedures reported in the previous paper.[6] These catalysts were analyzed as ZnO–$ZnFe_2O_4$ by means of X-ray analysis (Fe$K\alpha$ radiation). All the experimental data were obtained using catalysts with particle sizes of 0,75 mm (average, 0,5—1.0 mm).

Results and Discussion

The physical properties of the catalysts are summarized in Table 1. These catalysts possess micropores of about 20 Å in addition to macropores (Table 1).

The reaction between phenol and methanol was carried out at 375 °C. The time factor was 14.4 g-cat. h/mol-feed, and the catalysts in the calcination at 500 °C were used. The results of the reaction are shown in Tables 2a and 2b. As may be seen in Tables 2a and 2b, the catalysts selectively catalyze the methylation at the ortho position of phenol and simultaneously catalyze the decomposition of methanol. In order to

TABLE 1. PHYSICAL PROPERTIES OF THE ZnO–Fe_2O_3 CATALYSTS IN SEVERAL PREPARATIONS

Catalyst symbol	Starting materials (Zn–Fe)	Calcination temperature (°C)	Total pore volume (cm^3/g)	Surface area (m^2/g)	Pore[b] radius (Å)
A-5	O-O[a]	500	0.265	9.4	610
A-6	(Tableting)	600	0.294	7.5	720
A-7		700	0.276	5.8	960
A-8		800	0.192	5.3	1300
B-5	CO_3-O	500	0.442	35.0	150
B-6	(Extrusion)	600	0.418	18.8	250
B-7		700	0.373	15.0	290
B-8		800	0.308	5.5	700
C-5	O–OH	500	0.190	40.4	80
C-6	(Extrusion)	600	0.190	14.5	270
C-7		700	0.170	8.2	380
C-8		800	0.110	5.6	390
D-5	CO_3-OH	500	0.189	21.2	135
D-6	(Extrusion)	600	0.203	19.6	140
D-7		700	0.152	5.3	380
D-8		800	0.100	2.3	700
E-5	OH-OH	500	0.134	36.6	85
E-6	(Coprecipi-	600	0.126	12.6	175
E-7	tation)	700	0.058	3.3	215
E-8		800	0.013	—	—

a) Catalyst prepared from ZnO and Fe_2O_3. b) All catalysts have micropores of about 20 Å radius.

Table 2a. Reaction products in the reaction between phenol and methanol on various catalysts

Catalyst symbol	A-5	B-5	C-5	D-5	E-5
Phenol converted, mol%	16.4	21.3	55.9	26.5	54.0
Selectivity, %[a]					
o-Cresol	92.5	92.4	90.0	88.0	86.3
2,6-Xylenol	7.5	7.6	10.0	12.0	13.7
Methanol converted, mol%	27.3	26.8	52.8	28.0	43.7
Selectivity, %[b]					
Methylation	12.8	16.8	17.4	17.0	18.9
Decomposition	87.2	83.2	82.6	83.2	80.9

a) Defined by (mol of *o*-cresol or 2,6-xylenol per mol of converted phenol). b) Defined by (mol of methyl group in products or gaseous products per mol of converted methanol).

Table 2b. Compositions of gaseous products in the reaction between phenol and methanol over various catalysts

Catalyst symbol	A-5	B-5	C-5	D-5	E-5
Carbon dioxide, mol%	16.5	20.6	17.4	18.0	17.5
Hydrogen, mol%	56.4	51.6	60.8	58.9	59.7
Methane, mol%	23.9	20.9	12.3	14.5	15.2
Carbon monoxide, mol%	8.1	6.8	9.5	8.6	7.6

confirm the above results, the reaction between 2,6-xylenol and methanol was carried out on a (A-6) catalyst under the same reaction conditions. The experimental results showed that no methylphenol was produced. However, it was shown that methanol decomposed to form gaseous products similar to those shown in Table 2b. Therefore, it may be concluded that the overall reaction is a composite of the following two reactions:

$$\text{Phenol} + \text{Methanol} \xrightarrow{k_1} o\text{-Cresol} \longrightarrow \text{2,6-Xylenol} \qquad (1)$$

$$\text{Methanol} \xrightarrow{k_2} \text{Gaseous products} \qquad (2)$$

Phenol is consecutively consumed by Reaction (1), but methanol is consumed by Reactions (1) and (2).

In order to obtain available information on the preparative method of the most favorable catalyst, estimations of the individual rate constants were undertaken. For this purpose, the effects of the intraparticle diffusion on the observed rate should be clarified. The relation between the particle size and the activity of catalyst is shown in Fig. 1. The figure indicates that the effect of intraparticle diffusion is negligible. On the basis of this experimental result, the catalysts used for measuring the rate constant were crushed and sieved from 0.5 mm to 1.0 mm size.

The rate of the methylation was found to obey the following equation:

$$-\ln(1-f_p) = k_1(W/F) \qquad (3)$$

where f_p is the conversion of phenol.

However, as methanol is consumed by both methylation and decomposition, the rate of Reaction (2) should be expressed by the net conversion (f_m) of the decomposition of methanol. Therefore, the rate of the decomposition satisfies the following equation:

$$-\ln(1-f_m) = k_2(W/F) \qquad (4)$$

Arrhenius plots of k_1 and k_2 are given in Fig. 2, and the activation energies are summarized in Table 3.

The data summarized in Table 4 indicate that the activities of the catalysts used were not directly proportional to the surface area. Further, it may be suggested on the basis of Table 4 that the difference in the activities of these catalysts arises from the different starting materials and the various calcination tem-

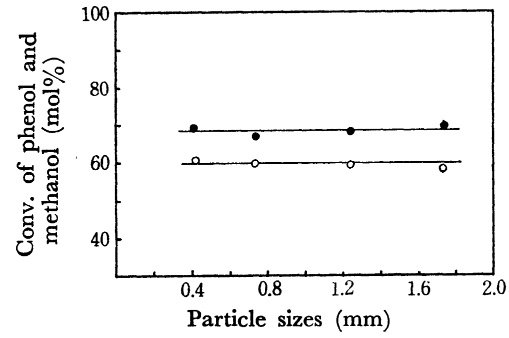

Fig. 1. Effects of particle sizes of the catalyst.
-○-: conversion of phenol
-●-: conversion of methanol
Conditions;
Reaction temp.; 375 °C
W/F; 35 g-cat. h/mol-feed
Reactants; methanol (5 mol)/phenol(1 mol)
Catalyst; A-5

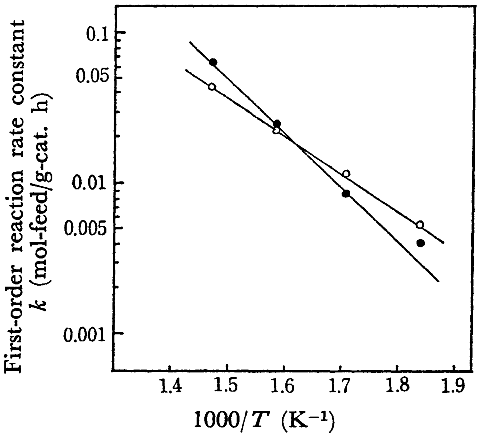

Fig. 2. Arrhenius plots of k_1 and k_2.
-●-: decomposition of methanol
-○-: conversion of phenol

Table 3. Activation energies of the methylation and the decomposition over the $ZnO-Fe_2O_3$ catalysts

Catalyst symbol	E_1 (kcal/mol)	$A_1 \times 10^{-6}$ (h^{-1})	E_2 (kcal/mol)	$A_2 \times 10^{-7}$ (h^{-1})
A-5	22.6	0.59	24.7	0.33
B-5	20.1	0.15	28.6	10.1
C-5	25.4	18.0	27.4	6.8
D-5	22.7	11.0	29.9	38.1
E-5	24.1	5.4	30.5	76.0

TABLE 4. FIRST-ORDER RATE CONSTANTS PER UNIT SURFACE AREA

Catalyst symbol	$k_1 \times 10^3$ (mol/m^2 h)	$k_2 \times 10^3$ (mol/m^2 h)
A-5	1.47	1.60
A-6	0.51	1.35
A-7	0.44	1.10
A-8	0.16	0.58
B-5	0.67	0.70
B-6	0.62	0.73
B-7	0.32	0.53
B-8	0.20	0.56
C-5	1.22	1.10
C-6	1.17	1.13
C-7	0.97	1.45
C-8	0.63	1.26
D-5	1.16	1.15
D-6	0.98	1.14
D-7	0.41	1.02
D-8	0.48	1.54
E-5	1.12	1.03
E-6	1.86	1.75
E-7	1.29	2.04
E-8	—	—

peratures. For example, although the (B) and (D) catalysts were both prepared from the one starting material of zinc carbonate (Table 1) and have nearly equal pore radii, the activities show a considerable difference, even at the same calcination temperature. The difference in the activities of the (B) and (D) catalysts may, therefore, be attributed to the difference in the starting material because the (B) catalyst was prepared from ferric oxide as the other starting material, while the (D) catalyst was prepared from ferric hydroxide. Moreover, the difference in the activities of the catalysts prepared from the same starting materials may be attributed to the difference in the calcination temperature. That is, the degree of the decrease in the rate of the methylation becomes considerably larger with the rise in the calcination temperature of the catalyst, while that of the decomposition is not so large.

These facts seem to indicate that the difference in the intrinsic activity of the catalysts resulted from the differences in the preparative method and in the calcination temperature.

According to Wheeler,[2] when the effects of the intraparticle diffusion is negligible, the selectivity factor (S) in a simultaneous reaction is defined as follows:

$$S = k_1/k_2 \qquad (5)$$

Since the rate constants in Table 4 were determined under negligible intraparticle diffusion, Eq. (5) was reasonably used for the estimation of the most favorable catalyst. The effects of the calcination temperature on the selectivity factor are shown in Fig. 3. The Figure shows that the selectivity factor is considerably affected not only by the calcination temperature, but also by the preparative methods. The selectivity factors of the (A) and (D) catalysts (S_a and S_d) decrease considerably with the rise in the calcination temperature, but S_b and S_c are comparatively stable at temperatures below 600 °C. Although the decrease in the selectivity factor occurs with the disappearance of the active sites for the methylation and/or creation of the active sites for the decomposition, it may be said on the basis of Table 4 that when the calcination temperature is higher, the concentration of the active sites for the methylation is smaller.

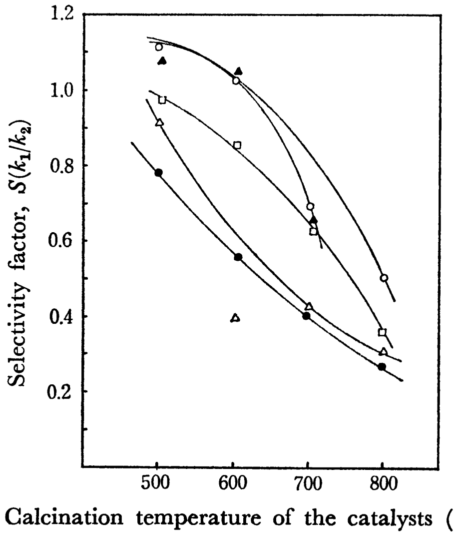

Fig. 3. Relations between the selectivity factor and the calcination temperature.
△: A, □: B, ○: C, ●: D, ▲: E.

Thus, it was concluded that the ZnO–Fe_2O_3 catalyst should be prepared at a low temperature. Further, it can be said that the catalysts for the methylation are effective in this order: (C), (E)>(B)>(D),(A).

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