Catalytic Properties of Metal Sulfates Supported on γ-Al_2O_3 in the Liquid-Phase Isopropylation of *m*-Cresol with Propylene

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γ-Al_2O_3 was impregnated with various metal sulfates, calcined, and used as catalysts in the liquid-phase isopropylation of *m*-cresol at 250—300 °C, with the propylene pressure in the range from 15 to 79 kg/cm^2. The catalytic activities of the sulfates were in the order: $Al_2(SO_4)_3 > ZnSO_4 \approx NiSO_4 > FeSO_4 > CuSO_4 > Li_2SO_4 \approx$ none $\approx CaSO_4 > Na_2SO_4$. The order of the selectivity ϕ for *ortho*-isopropylation over *para*-isopropylation was opposite to that of the catalytic activity. $FeSO_4/Al_2O_3$ catalysts resulted in the best ϕ value and fairly high activity, which were independent of the calcination temperature over the range of 300—500 °C. The formation of Brønsted acidic sites with $1 \leq H_0 \leq 3$ as catalytically-active sites was estimated for the $FeSO_4/Al_2O_3$ and $ZnSO_4/Al_2O_3$ catalysts.

In the past few years,[1)] the present authors have studied the use of solid catalysts in the liquid-phase isopropylation of *m*-cresol (I) with propylene (IV) for the preparation of thymol (II), which is an important starting material for menthol. Solid acids, such as silica–alumina and $Al_2(SO_4)_3$, showed high catalytic activity, but the selectivity for *ortho*-isopropylation (ϕ) was not high enough to suppress the formation of 4-isopropyl-5-methylphenol (III) to within the industrial requirements. On the other hand, γ-Al_2O_3 and solid bases such as CaO showed high ϕ values, but were of insufficient catalytic activity.[1b)] When some metal sulfates were supported on γ-Al_2O_3, the resultant solids were found to catalyze the reaction with high efficiency and a high ϕ value.[1a)] Yet, little has been studied of their catalytic actions. Later, some interesting results were presented on the catalytic activity of supported metal sulfates (on γ-Al_2O_3 and SiO_2) in the vapor phase isopropylation of I with IV.[2a)] In this case, the distribution of products other than thymol was different from that in the liquid-phase isopropylation, and therefore, these results are not helpful in the estimation of the catalytic action in the liquid phase.

In this paper, the catalytic properties of various metal sulfates supported on γ-Al_2O_3 are reported for liquid-phase isopropylation, and compared with the recent investigations on the properties of supported sulfates.[2—6)]

Experimental

Preparative Procedure of the Catalysts (A). The desired amount of a metal sulfate was dissolved in distilled water, and 75 g of γ-Al_2O_3 (Nikki Chemicals Co., Ltd.; BET surface area: 205 m^2/g) of 100—200 mesh was added to the solution. Na_2SO_4, $Li_2SO_4 \cdot H_2O$, $CaSO_4 \cdot 1/2H_2O$, $ZnSO_4 \cdot H_2O$, $CuSO_4$, $Al_2(SO_4)_3$, $FeSO_4 \cdot 7H_2O$, and $NiSO_4 \cdot 7H_2O$ of guaranteed reagent grade were used. The weight of the dissolved sulfate in the anhydrous state was 25 g. After standing for 15—16 h, the impregnated solid was filtered, and washed with 200 ml of distilled water 3 times. The resultant solid was evaporated to dryness on a water bath, and calcined at 500 °C for 4 h. No particular attention was paid to exclude traces of moistures.

Preparative Procedure of the Catalysts (B). Before filtration in the above procedure, the suspension of the impregnated solid in the sulfate solution was concentrated, evaporated to dryness and calcined. In this case, the impregnated amount of the sulfate was expressed in wt% based on the weight of the dissolved sulfate in the anhydrous state against the resultant catalyst.

Surface Acidity of the Catalysts. The acid-base strength distribution of the catalysts were measured by a titration method.[7)]

Analysis of $FeSO_4/Al_2O_3$ Catalysts. 0.5 g of the catalyst was dissolved in 25 ml of H_3PO_4 and 10 ml of 33 wt% H_2SO_4 by heating in a CO_2 stream. The iron(II) content was determined by titrating the solution with $KMnO_4$ at room temperature.[8a)]

The iron(II) in an extract of the catalyst with dil. HCl was oxidized into iron(III) by HNO_3.[9)] The total iron content was determined by titration in the presence of a Variamine Blue B Base which was used as an indicator.[10)]

The SO_4^{2-} content in the HCl extract was determined based on the amount of $BaSO_4$ precipitate which had been separated using an ordinary procedure.[8b)]

Reaction Procedure (A). The isopropylation of I with IV was carried out in the liquid phase without solvents in an autoclave of 100 ml volume. The IV pressure (P) was maintained constant with the incremental addition of IV. The amount of catalyst (W) was 15 wt% with respect to the initial amount of I.

Reaction Procedure (B). The liquid-phase isopropylation of I was also carried out without the incremental addition of IV. The initial mole ratio IV/I was 3.0. W was 5 or 15 wt% with respect to the initial amount of I.

Products Analysis. After the desired reaction period, the autoclave was cooled rapidly to room temperature in a cold water stream. After the unreacted IV had been released, the reaction mixture was dissolved in ether. The ether solution was washed with water, dried over Na_2SO_4 and concentrated.

Then the reaction mixture was analyzed using gas chromatography, with a Kotaki Model GU-21A on a 2 m × 5 mmϕ column packed with 20 wt% of silicone oil (D.C. 200) on Celite-545 (60—80 mesh). The column temperature was 165 °C, and He was used as the carrier at 1.2 kg/cm^2. Some of the reaction mixture were fractionated into components by a modified fractional gas chromatograph, and each component was identified by the IR absorption spectrum in a Nujol mull.

Results and Discussion

The products of the isopropylation were thymol (II; main product), 4-isopropyl-5-methylphenol (III), 2,6-diisopropyl-5-methylphenol, 2,4-diisopropyl-5-methyl-

TABLE 1. EFFECTS OF THE IMPREGNATED AMOUNT OF SULFATESa)

Impregnated amount (wt%)	$ZnSO_4/Al_2O_3$b)				$FeSO_4/Al_2O_3$c)	
	θ (min)	x (mol%)	ϕ (mol%)	Acidity of $1 \leq H_0 \leq 3$ (meq/g)	x (mol%)	ϕ (mol%)
0	240	11	100	0		
0.5				0		
5					15	100
10					66	86
20	20	83	79	0.8	87	78
30					74	79
40	50	79	74	0.07	29	100
80	100	81	74	0.04		
100					11	100

a) Catalysts were prepared using Procedue B; calcined at 300 °C for 4 h. b) Reaction Procedure B was employed at 250 °C. c) Reaction Procedure A was employed at 260 °C for 20 min.

TABLE 2. EFFECTS OF SULFATES ON CATALYTIC PROPERTIES

Catalyst	Reaction proceduree)	t (°C)	θ (min)	x (mol%)	ϕ (mol%)	S
$Al_2(SO_4)_3/Al_2O_3$b)	B	250	1	96	72	4.53
$ZnSO_4/Al_2O_3$b)	B	250	8	83	79	4.53
$NiSO_4/Al_2O_3$b)	B	250	12	84	76	4.30
$FeSO_4/Al_2O_3$b)	B	260	20	87	78	4.31d)
$CuSO_4/Al_2O_3$b)	B	300	10	97	76	4.47
$CaSO_4/Al_2O_3$b)	B	300	240	73	93	3.93
Li_2SO_4/Al_2O_3b)	B	300	240	81	89	2.89
Na_2SO_4/Al_2O_3b)	B	300	240	28	100	2.84
$Al_2(SO_4)_3/Al_2O_3$a)	A	260	10	95	81	4.53
$ZnSO_4/Al_2O_3$a)	A	260	10	94	87	4.53
$NiSO_4/Al_2O_3$a)	A	260	10	94	85	4.30
$FeSO_4/Al_2O_3$a)	A	260	10	67	93	4.31d)
$FeSO_4/Al_2O_3$a)	A	260	30	94	94	4.31d)
$CuSO_4/Al_2O_3$a)	A	260	10	5	100	4.47
γ-Al_2O_3	B	300	240	84	86	3.74
γ-Al_2O_3	B	250	240	11	100	3.74

a) Impregnated using Procedure A; calcined in N_2 at 500 °C for 4 h. b) Impregnated with a sulfate of 20 wt% using Procedure B; calcined in air at 300 °C for 4 h. c) P was 25 kg/cm^2 using Procedure A. Following Procedure B, $P_{\text{at } \theta=0}$ was 65 kg/cm^2 at 250 °C and 79 kg/cm^2 at 300 °C. d) The S value of $Fe_2(SO_4)_3$ was 4.49.

phenol, a small amount of isopropyl *m*-tolyl ether (I_e), and also a small amount of the isopropyl ethers of the products. No 6-isopropyl-5-methylphenol, 3-isopropyl-5-methylphenol, or isothymol were found as products. The kinds and distributions of the by-products are obviously different from those resulting from vapor-phase isopropylation.2)

The catalytic properties of the supported catalysts are presented in Tables 1 and 2, where t, P, θ, x, ϕ, and S respectively denote the reaction temperature, pressure of IV, reaction time, conversion of I, selectivity for *ortho*-isopropylation, and electronegativity of the sulfate supported or of Al_2O_3. ϕ was defined as the ratio, $100 \times$ {total *ortho*-isopropylated products}/{total isopropylated products excepting I_e}. The catalytic activities were compared to each other in terms of x, θ, or t. The impregnated amount of a sulfate due to Procedure A was estimated to be less than 10 wt%. The amount of $FeSO_4$ impregnated using Procedure A varied from 3 to 8 wt%, which was determined from the Fe content of the $FeSO_4/Al_2O_3$ catalysts in a series of preparative runs. The values of S were calculated on a relative compactness scale in terms of the Sanderson method.11)

Catalytic Activity. From Table 1, the activities of catalysts prepared by Procedure B appear to have maximum values for an impregnated amount of *ca.* 20 wt%. It can be deduced from Table 2 that the effect of the sulfate on the activity of the catalysts follows the order: $Al_2(SO_4)_3 > ZnSO_4 \approx NiSO_4 > FeSO_4 > CuSO_4 > Li_2SO_4 \approx$ none $\approx CaSO_4 > Na_2SO_4$.

It is noted that this order holds for both catalysts prepared following Procedure B with 20 wt%-impregnation, as well as those following Procedure A.

Moreover, this is consistent with the order of activities of catalysts supported with various sulfates and calcined at arbitrary temperatures in reaction involving the protonation of olefins, namely, $Al_2(SO_4)_3 > NiSO_4 > BeSO_4 > Li_2SO_4 >$ none over SiO_2 and $Al_2(SO_4)_3 > BeSO_4 > NiSO_4 > MgSO_4 >$ none $> Li_2SO_4 \approx Na_2SO_4$ over γ-Al_2O_3 in the vapor-phase isopropylation of *m*-cresol with propylene,2a) $MnSO_4 > ZnSO_4 > Cr_2(SO_4)_3 >$

$CuSO_4$>none over silica–alumina in the vapor-phase ethylation of benzene with ethylene,[5] and $Al_2(SO_4)_3$> $ZnSO_4$>$MnSO_4$>K_2SO_4 over silica gel in the vapor-phase hydration of propylene.[4]

Whereas the catalytic activities of unsupported sulfates are sensitive to the preparative conditions such as the calcination temperature,[12] it will be remarked that these orders are almost the same. In these studies, catalytic actions are estimated to involve the protonation of propylene or ethylene,[3–5] and the sulfates are estimated to affect the catalytic activities as a source of acidic sites of the Brønsted type.[2–5] It follows that the relative catalytic activity of the supported catalyst depends on the intrinsic properties of the sulfates.[6] The electronegativity S represents the power of individual atoms in a molecule to attract electrons. Therefore, the acid strength of the molecule can be expressed, to a first approximation, by the value of S: the greater S, the stronger the electron accepting power.[11] Table 2 shows that the order of the activities of supported catalysts or γ-Al_2O_3 is much the same as the order of the S values. The catalytic activity of the supported catalyst appears to depend predominantly on the acid strength of the sulfate.

It will be deduced from Table 2 that only sulfates having the S values greater than that of γ-Al_2O_3 are effective in improving the catalytic activity of γ-Al_2O_3 by the support.

Selectivity. In Table 2, the order of selectivities ϕ is just the opposite to that of the activities, namely, the greater the S of the sulfate, the lower the ϕ of the supported catalyst. The ϕ of a catalyst does not vary with x or θ. This is interpreted as follows.

Phenols have been known to be adsorbed *via* their OH groups, on basic sites of a catalyst.[2,13] No acidic site with $H_0 \leq 6.8$ but basic sites whose conjugate acids had H_0 values less than 7 were observed on γ-Al_2O_3 used as the carrier.[7] Over the supported catalysts, *m*-cresol (I) was adsorbed either on the basic sites of γ-Al_2O_3 when they are exposed, or on the basic sites of the supported sulfate when the sulfate covered the entire surface of γ-Al_2O_3. (Even if the surface possesses strong acidic sites, the coexistence of weak basic sites is reasonable.[14]) Isopropylation occurs between the isopropyl cations formed on the Brønsted acidic sites[5] and the I adsorbed on the basic sites.[2] When the vicinity of the basic sites is strongly acidic, the aromatic ring of I orients itself coplanar to the surface because of the interaction between π-electrons and the surface. On the other hand, when the vicinity of the basic sites is basic, the aromatic ring is tilted upward such that the para position is farther from the surface than the ortho position because of the electrostatic repulsion between the π-electrons and the surface.[13,15] Then, the attack of the isopropyl cation from the surface to the para position is retarded by means of resistance to the transfer of the cation or by means of reduced entropy change. Thus, ϕ increases for a decrease in the acid strength in the vicinity of the basic sites according to a similar scheme as has often been remarked for selectivity in the alkylation of phenols.[15]

Because the acid strength of the surface is predominantly affected by the acid strength of the sulfate,[3] the order of ϕ can be interpreted from the above discussion. In confirmation, the present author found that the apparent activation energy about the rate constant (first order with respect to I) in the formation of 4-isopropyl-5-methylphenol was lower by *ca.* 16 kcal/mol than the formation of thymol. In addition, the higher ϕ value of the catalysts prepared following Procedure A than those prepared by Procedure B in Table 2 are interpreted as being due to the basicity of the exposed γ-Al_2O_3.

It was pointed out by Nitta *et al.*[2a] that the selectivity of thymol formation did not depend on the kind of sulfate supported on γ-Al_2O_3 in the vapor phase isopropylation of I. It should be noted that their definition of the selectivity is quite different from ϕ in the present report and does not indicate the effect of the relative reactivities at the *ortho* and *para* positions.

$FeSO_4/Al_2O_3$ Catalyst. From Table 2, the catalyst impregnated with $FeSO_4$ (labelled the "$FeSO_4$/Al_2O_3 catalyst") will be distinguished from other catalysts in respect of its excellent ϕ value and fairly high catalytic activity, The selectivity of thymol over the catalyst was as high as 74—86 mol% of the total products in the reactions presented in Table 2 and in Fig 3. When heated in the atmosphere, hydrated $FeSO_4$ is known to convert into $Fe_2(SO_4)_3$, $(Fe_2O_3)_n\cdot(SO_3)_m$ (basic iron sulfates), or Fe_2O_3.[15] Most of the Fe was found to be Fe(III) and the ratio, $\{SO_3$ and/or $SO_4^{-2}\}$/Fe(III), was found to be 0.8—1.1 upon analysis of the catalyst prepared by Procedure A. The necessity of SO_3 or SO_4^{2-} for the catalytic action was supported by the fact that a catalyst impregnated with $Fe(OH)_3$ instead of $FeSO_4$ was virtually inactive. Consequently, the $Fe_2O_3\cdot(SO_3)_2$ or $\{Fe_2(SO_4)_3\}_2\cdot Fe_2O_3$ was postulated to arise from the $FeSO_4$ participating in the catalytic action.

The catalytic activity and the selectivity ϕ were not affected by the calcination temperature to within 300—500 °C, as is shown in Fig. 1. These insensitivities satisfy the industrial requirements of stable catalytic

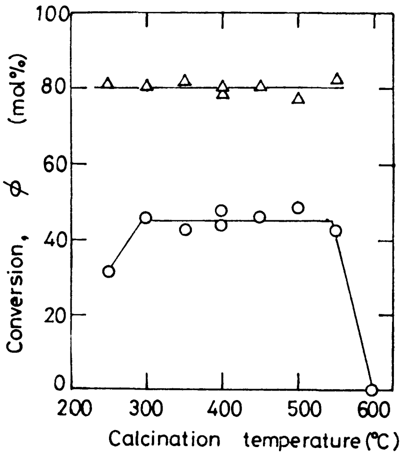

Fig. 1. Effects of calcination temperature on activity and ϕ of $FeSO_4/Al_2O_3$ catalysts prepared by Procedure B. γ-Al_2O_3 were impregnated with $FeSO_4$ by 25 wt% and calcined in air for 4 h. ○: Conversion, △: ϕ. Reaction Procedure B was employed at 260 °C, for 20 min, with W=5 wt%.

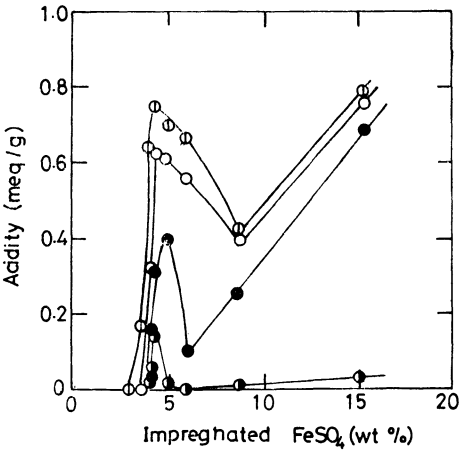

Fig. 2. Acidities of $FeSO_4/Al_2O_3$ catalysts prepared by Procedure A. ⦶, $H_0 \leq 4$; ○, $H_0 \leq 3.3$; ●, $H_0 \leq 1.5$; ◑, $H_0 \leq -3$.

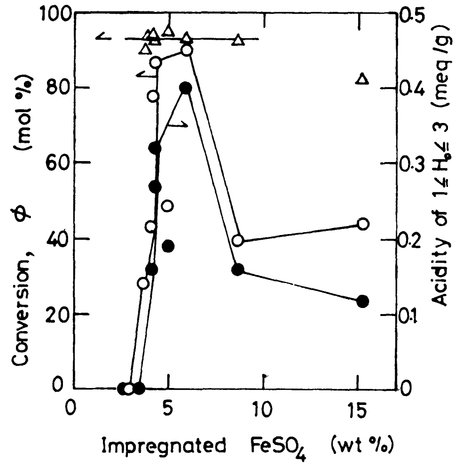

Fig. 3. Effects of impregnated amount on catalytic activity, ϕ, and the acidity of $1 \leq H_0 \leq 3$ over $FeSO_4/Al_2O_3$ catalyst prepared by Procedure A. Reaction Procedure A was employed at 260 °C, for 15 min, with $P = 15$ kg/cm^2. ○: Conversion, △: ϕ, ●: acidity of $1 \leq H_0 \leq 3$.

properties. It has been remarked that the acidic properties of metal sulfates are sensitive to the calcination temperature, and especially the strongest acidic sites on the surface can exist only for a particular calcination temperature with sufficient care being taken to exclude traces of moisture.[2–4,6] Therefore, catalytic activity greatly depends on the calcination temperature when the strongest acidic sites prevail in the catalytic action.[6]

Figure 1 suggests that the active acidic sites on $FeSO_4/Al_2O_3$ are not so strong. The acidities of the catalysts over various H_0 ranges are shown in Fig. 2. The catalyst impregnated with 15 wt% $FeSO_4$, presented in Figs. 2 and 3, was prepared following Procedure A without the washing process. In Fig. 3, the catalytic activity and the acidity for $1 \leq H_0 \leq 3$ indicate correlations exactly in parallel to the impregnated amount and have maximum values for an impregnated amount of about 6 wt%. (The acidities for $1 \leq H_0 \leq 3$ were determined from acid-strength distribution curves correlating the acidities, shown in Fig. 2, the H_0 values.) Then, acidic sites with $1 \leq H_0 \leq 3$ are postulated to be active in the present reaction and to arise most efficiently from $FeSO_4$ at an impregnated amount of about 6 wt%. The strength of the acidic sites will be affected by the interaction between γ-Al_2O_3 and the species arising from $FeSO_4$.

Provided that the acidic sites of a particular H_0 range arise from a particular surface structure, sites on γ-Al_2O_3, where $FeSO_4$ is adsorbed by impregnation and are converted into acidic sites with $1 \leq H_0 \leq 3$, are considered to be filled to an impregnated amount of about 6 wt%. Above this value, the surface of the γ-Al_2O_3 will be occupied by $FeSO_4$ in a scheme different from lower impregnated amounts, which reduces the exposed γ-Al_2O_3 on the surface in the vicinity of the individual adsorbed $FeSO_4$, where efficiency of the $FeSO_4$ for acidic sites, with $1 \leq H_0 \leq 3$ is lowered and instead the efficiency for acidic sites of other types is increased. The catalytic action of acidic sites with $1 \leq H_0 \leq 3$ are interpreted by their arrangement toward the basic sites of γ-Al_2O_3 in the most suitable structure so that isopropyl cations easily attack the adsorbed I. The constant high ϕ value for impregnated amounts less than 9 wt% in Fig. 3 is supported by the basic property of the exposed γ-Al_2O_3 in the vicinity of the acidic sites. While the lower ϕ value at an impregnated amount of about 15 wt% implies a higher coverage of γ-Al_2O_3.

If acidic sites with $1 \leq H_0 \leq 3$ protonate propylene as do the acidic sites over the supported sulfate catalysts,[2–4] they are Brønsted acidic sites.

It is suggested from Table 1 that the active acidic sites on the $ZnSO_4/Al_2O_3$ catalyst are of $1 \leq H_0 \leq 3$. Though, it cannot be deduced that strength of the active sites on the other catalysts in this study are the same, the stronger H_0 range of the sites may not be in contradiction when the sulfate of the stronger acidity, such as $Al_2(SO_4)_3$, is supported.

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