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The Alkylation of *m*-Cresol with Propylene by Supported Metal Sulfates

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Synopsis. The alkylation of *m*-cresol with propylene over supported metal sulfate catalysts was studied at 250 °C under atmospheric pressure. The activity of the catalyst varied with the kind of sulfate and the calcination temperature, whereas the selectivity to thymol was independent of those factors and depended on the type of carrier instead.

The alkylates of phenols are quite often useful for the processing of raw materials related to perfumery, antiseptics, dyes, and synthetic resins.[1] Thymol (2-isopropyl-5-methylphenol), an important raw material in perfumery, is usually obtained by the liquid-phase reaction of *m*-cresol and propylene in the presence of an acidic catalyst; alkylation in the vapor phase is rare,[2] except for one patent.[1a] Moreover, the details of the catalysis in that patent are unclear.

In this paper, the vapor-phase alkylation of *m*-cresol with propylene over supported sulfate catalysts will be reported in order to clarify the factors governing the activity and the selectivity for thymol formation.

The propylene was obtained from the Mitsubishi Petrochemical Co., Ltd. Commercial *m*-cresol was purified by distillation under reduced pressure; its purity was estimated to be over 99.5% by means of gas chromatography. Porous silica-gel (Davison RD gel) and activated alumina (Nishio Industies Co., Ltd., KHD-24) were used as the catalyst carriers. The sulfates were guaranteed reagents purchased from the Kanto Chemical Co., Inc. Each sulfate was 1.0 mmol per unit of weight of the carrier. All the catalysts were prepared by impregnating the carrier with an aqueous solution of a sulfate for a day and then by drying it at 120 °C in the air. It was assumed that all of the sulfate was supported on the carrier.

The activity test was carried out in a flow system under atmospheric pressure. A catalyst (10—20 mesh) packed in a glass tube reactor was activated at a given temperature for 3 hr in a nitrogen stream before the reaction. The liquid products, which were collected every 20 min, was analyzed by gas chromatography with a column containing lanolin (5 wt%) and LAC (0.5 wt%) supported on Chromosorb AW (2 m, 145 °C).

The acidic properties of the catalysts were measured by the usual *n*-butylamine titration using the Hammett indicators. The surface areas of the catalysts were measured by the BET method.

In this alkylation, the liquid products obtained were thymol and its three isomers, *iso*-thymol, and a small quantity (3 mol%) of an unknown component.* Among those products, the thymol (obtained in a *ca.* 70% yield) is the most desirable, as has been mentioned above. The initial conversion of *m*-cresol by extrapolation to zero time was taken as the catalytic activity, for the conversion decreased gradually with the time. The selectivity of the catalyst was expressed by the ratio of the thymol to all of the thymol isomers, and it was held constant throughout the time on stream. The activities and the selectivities of the various catalysts are shown in Table 1. The activities of the carriers were poor, though they were measurable. It is clear that the addition of the sulfates, with the exception of the Li and Na salts, increases the activity of the carrier. The activity varied with the kind of sulfate. These catalysts gave a high selectivity for thymol formation, though it was difficult to ascertain the equilibrium composition of thymol isomers. The activities seem to have no direct relation to the surface areas. The silica-carrier catalysts showed a selectivity of *ca.* 70%, while the alumina-carrier catalysts showed one of *ca.* 60%. From these facts it can be considered that the activity depends upon the property of the sulfate and that the selectivity depends upon the property of the carrier.

Metal sulfate is a well-known solid acid and catalyzes various reactions.[3] Fukui *et al.* have reported that the sulfates supported on silica-alumina are effective for the ethylation of benzene.[4] They supposed that the modified acid sites of the sulfate produced on the carrier are responsible for the activity. Therefore, the acidities of the present catalysts were measured (Tables 1 and 2). A rough correlation between the acidities (the amount of acid sites having the strength with $H_0 \leqq +3.3$) and the activities was found for a series of catalysts of a given carrier. In spite of its higher acidity, the acid sites of both carriers seem to be ineffective for the alkylation. These facts support Fukui's

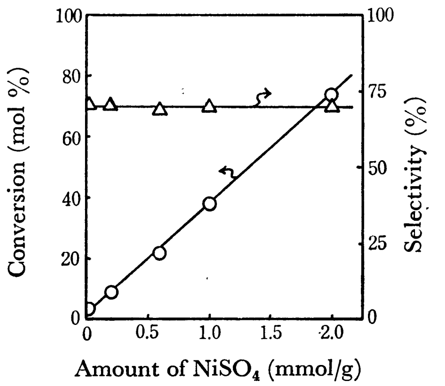

Fig. 1. Effect of supported amount of NiSO$_4$ on SiO$_2$. Conditions: W/F = 19.5 g·hr/mol, reaction temp. = 250 °C, calcination temp. = 300 °C, propylene/*m*-cresol = 1.0 mol/mol.
○: *m*-cresol conversion, △: thymol selectivity.

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* We assumed the relative mole sensitivity of the unknown to be the same as those (0.78) of the thymol isomers to *m*-cresol.

TABLE 1. ACTIVITIES AND ACIDITIES OF SUPPORTED METAL SULFATE CATALYSTS

Catalyst[a)]	Conversion[b)] (mol %)	Selectivity (%)	Acidity, (mmol/g) $H_0 \leqq -3.0$	$H_0 \leqq +3.3$	Surface area (m^2/g)
SiO_2 (small pore)	4.0	67	0.20	0.61	817
Li_2SO_4–SiO_2	5.0	69	0.20	0.32	—
Na_2SO_4–SiO_2	0	—	0	0.26	744
$BeSO_4$–SiO_2	30	69	0.06	0.56	—
$MgSO_4$–SiO_2	27	69	0.09	0.48	—
$NiSO_4$–SiO_2	37	70	0.03	0.69	731
$Al_2(SO_4)_3$–SiO_2	47	69	0.60	0.69	—
Al_2O_3	0.1	57	0	0.34	326
Li_2SO_4–Al_2O_3	0	—	0	0	—
Na_2SO_4–Al_2O_3	0	—	0	0	312
$BeSO_4$–Al_2O_3	37	60	0	0.14	—
$MgSO_4$–Al_2O_3	1.2	60	0	0.05	—
$NiSO_4$–Al_2O_3	2.8	56	0	0.12	302
$Al_2(SO_4)_3$–Al_2O_3	42	56	0	0.35	—

a) Supported amount = 1.0 mmol/g, Calcination temp. = 300 °C. b) Reaction conditions: Temp. = 250 °C, W/F = 19.5 g·hr/mol, propylene/*m*-cresol = 1.0 (mol/mol).

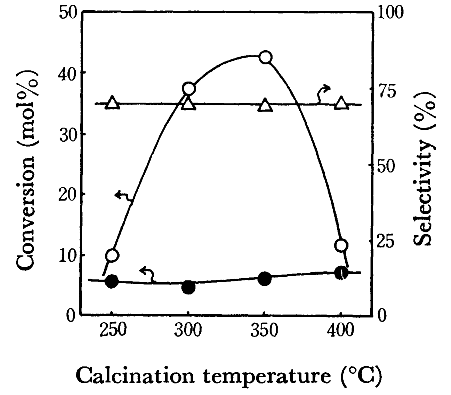

Fig. 2. Effect of calcination temperature of catalyst. Catalyst: $NiSO_4$–SiO_2, Conditions are the same as those in Fig. 1.
○: *m*-cresol conversion of $NiSO_4$–SiO_2, ●: *m*-cresol conversion of SiO_2, △: thymol selectivities of SiO_2 and $NiSO_4$–SiO_2.

proposal. Furthermore, the fact that the activity per unit of weight of the catalyst increased with the $NiSO_4$ content, as is shown in Fig. 1, supports the idea that the effective active sites arise essentially from the sulfate. This has also been domonstrated by the effect of the calcination temperature on the activity, as is shown in Fig. 2. That is to say, the activity of $NiSO_4$–SiO_2 varied with the calcination temperature, though the activity of the carrier itself did not vary. This curve, having its maximum at 350 °C, agrees well with the variation in the acidity of heat-treated $NiSO_4$ which was previously determined by one of present authors and others.[5,6)]

The selectivity was held constant in Figs. 1 and 2, independent of the supported amount of sulfate and of the calcination temperature, as would be expected when the carrier was the same. Further, in order to elucidate the selectivity, a few typical solid acid catalysts were tested. The results, shown in Table 2, reveal that the selectivity is not governed by the acid strength of the catalyst. The selectivity of large-pore SiO_2 (80—100 Å) in Table 2 is lower than that of small-pore SiO_2 (22 Å) in Table 1. This suggests that, on the small-pore catalysts, the reactant molecules take a particular adsorbed state favorable to thymol formation. Details of the selectivity will be reported, along with data on other catalysts, at a later date.

TABLE 2. ACIDITY AND SELECTIVITY OF VARIOUS ACID CATALYSTS

Catalyst	Acidity (mmol/g) $H_0 \leqq -3.0$	$H_0 \leqq +3.3$	Conversion[d)] (mol%)	Selectivity (%)
SiO_2(large pore)	0.10	0.14	2	62
SiO_2–Al_2O_3[a)]	0.20	0.29	14	48
H_2SO_4–Al_2O_3[b)]	0.37	0.50	25	63
H_3PO_4–celite[c)]	0.48	0.58	30	45

a) Commercial catalyst obtained from the Japan Gasoline Co., Ltd. b) Supported amount of H_2SO_4 = 1.0 mmol/g. c) Commercial solid phosphoric acid obtained from the Japan Gasoline Co., Ltd. d) Reaction conditions are the same as Table 1.

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