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ALKYLATION OF PHENOL WITH METHANE OVER SOLID ACIDS AND BASES

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The alkylation over SiO_2-Al_2O_3, SiO_2-TiO_2, Al_2O_3, MgO or MgO-Al_2O_3 was carried out at 400-500°C and atmospheric pressure. Though SiO_2-TiO_2, MgO and MgO-Al_2O_3 were catalytically inactive, Al_2O_3 formed 4-8% cresols and about 1% xylenol, while SiO_2-Al_2O_3 gave 1-3% cresols and 3.5% xylenols together with 7-14% diphenylether.

No work has been reported on the alkylation of phenol with methane, although work has been done on the alkylation of phenol with olefins or alcohols.1) The reaction of methane with benzene is known to take place over SiO_2-Al_2O_3 at 600°C and 232 atm. to give 4.6% toluene and 3.0% biphenyl.2) In the present work, we examined the extent of reaction of methane with phenol over several solid acid and base catalysts.

The reaction was carried out at 400 and 500°C by a standard flow method and the reaction products which were condensed by an ice trap were analyzed by gas chromatography with a column of silicone D.C. 550-Shimalite. The amounts of flowing phenol and methane were measured by a microfeeder and orifice flow meter respectively. The alumina used was KAT 6 of Nishio Chemical Co. and the silica-alumina was N631(L) (Al_2O_3:15%) supplied by Nikki Chemical Co. Both catalysts were calcined in air at 510°C for 3 hr. Magnesia was prepared by calcining basic magnesium carbonate at 700°C for 3 hr. Silica-titania (molar ratio=3:7) was prepared by calcining at 510°C a washed and dried coprecipitated mixture which was obtained by adding ammonia water to a solution of ethylsilicate and titanium tetrachloride. Magnesia-alumina (molar ratio=6:1) was prepared as reported previously3) and calcined in air at 510°C for 3.5 hr. The phenol was a guaranteed reagent of Wako Pure Chemical Co. and the methane, supplied by Takachiho Chemical Co., was dried by passing through a silica gel tube.

Table 1 shows the % yield of the reaction products together with the reaction conditions. Over the SiO_2-Al_2O_3 catalyst which has high acid strength, diphenyl ether was predominantly formed by the intermolecular dehydration of phenol. However, comparatively large amounts of cresols were found to form over Al_2O_3. The conversion % over Al_2O_3 increased as the molar ratio of methane to phenol decreased or as the temperature increased. Over both catalysts, 3,4-xylenol was formed at 500°C. Magnesium oxide, which has a basic character4) and is active and highly selective for the alkylation of phenol with methanol,5) and magnesia-alumina, which has both acidic and basic properties3) were almost inactive for this reaction. Silica-titania, which has similar acidic property6) to silica-alumina, did not show any catalytic activity.

The acidic and basic nature of the catalysts does not seem to correlate with the activity or the selectivity for this reaction, though some correlation were observed for alkylation with olefins or alcohols.1) However, it is striking that over alumina, phenol was alkylated appreciably with methane without any formation of diphenylether at atmospheric pressure.

Table 1 Molar % of products in the reaction of phenol with methane

	Catalysts	SiO_2-Al_2O_3		Al_2O_3			MgO	SiO_2-TiO_2	MgO-Al_2O_3
	Reaction temp., °C	400	501	410	400	507	505	410	401
	Catalyst amount, g	2.00	2.02	2.31	2.05	2.04	2.19	2.06	1.97
	Contact time, g-sec-ml^{-1}	3.10	2.71	3.78	3.08	2.86	3.07	3.24	3.12
	Molar ratio, CH_4:C_6H_5OH	1.03	1.05	0.89	5.0	0.94	0.94	0.98	0.99
Molar % of Products*	o-cresol	0.4	1.3	3.5	2.0	1.8	trace	0	0.7
	m,p-cresol	0.5	2.0	4.9	3.0	2.5	trace	0	trace
	3,4-xylenol	0	3.5	trace	0	1.3	0	0	0
	diphenylether	6.7	14.2	0	0	0	0	0	0
	unreacted	92.4	79.0	91.6	95.0	94.4	100	100	99.3

*) In all experiments, very small amounts of benzene and toluene were detected.

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