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HYDROALKYLATION OF BENZENES WITH Pd-Al_2O_3 AND NaCl-$AlCl_3$

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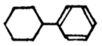
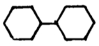
The synthesis of cyclohexylbenzenes by the hydroalkylation of benzene and toluene with a binary catalyst system was studied under various conditions. Using a catalyst of NaCl-$AlCl_3$(fused salts) as an alkylation catalyst and 0.24%Pd-Al_2O_3 as a reduction catalyst, cyclohexylbenzene(54.7 mol%) was obtained at 140°C for 5 hr under the presence of hydrogen. Further, the activity and the selectivity of hydroalkylation were also examined with several combined catalysts of noble metals and fused salts.

Cyclohexylbenzene is used for the preparation of phenol and cyclohexanone by the catalytic oxidation.$^{1)}$ In the alkylation of benzene with cyclohexene in the presence of an excess amount of anhydrous aluminum chloride, both cyclohexylbenzene and polycyclohexylbenzenes such as 1,4-dicyclohexylbenzene, 1,3,5-tricyclohexylbenzene and 1,2,3,5-tetracyclohexylbenzene are formed.$^{2)}$ Recently, the direct and selective synthesis of cyclohexylbenzene by the hydroalkylation of benzene has been investigated. For examples, using nickel-tungsten supported on fluorine containing SiO_2-$Al_2O_3$$^{3)}$ and 5%Ni-SiO_2-$Al_2O_3$$^{4)}$, cyclohexylbenzene was prepared in high selectivity by the hydroalkylation of benzene. In the latter catalyst, the yield of cyclohexylbenzene was 30.9%. Such catalysts as palladium supported on zeolite$^{5)}$ and ruthenium on acid-clay modified by hydrofluoric acid$^{6)}$ have been also used for this reaction. In the hydroalkylation of benzene, both hydrogenation catalyst and alkylation catalyst are inevitable. At first, authors examined a system of Pd-Al_2O_3 and $AlCl_3$. But, a small amount of aluminum chloride disturbed the hydrogenation on Pd-Al_2O_3. Then, it was found that a catalyst system of Pd-Al_2O_3 and fused salts(NaCl-$AlCl_3$, 1:1 molar ratio), which is insoluble in benzene, showed an excellent activity and selectivity for the hydroalkylation without disturbance of hydrogenation. In this paper, the catalytic properties in the hydroalkylation of benzene and toluene are studied.

30g of benzene, 1g of 0.24%Pd-Al_2O_3 and 3-4g of fused salts, which was prepared from anhydrous aluminum chloride and sodium chloride($Na^+AlCl_4^-$)$^{7)}$, are put in an autoclave(sus-32, 100ml volume) equipped with an electromagnetic stirrer. The autoclave was heated at 80-200°C under the hydrogen pressure of 100-150Kg/cm^2 for 1-20 hr. The reaction products were analyzed by gaschromatography, and identified by their retention time, IR, UV, NMR spectra and elementary analysis. The results of the hydroalkylation of benzene with binary catalysts were shown in Table 1.

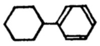
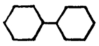
Table 1. Hydroalkylation of benzene with various noble metals and $NaCl\text{-}AlCl_3$

Cata. (g)	Temp. (°C)	Time (hr)	Yield(%)		
					
0.24%Pd-Al_2O_3(1)	105	5	20.5	36.9	0.6
0.24%Pd-SiO_2-Al_2O_3(1)	105	10	28.4	20.3	1.2
0.24%Pd-C(1)	105	10	10.1	7.2	1.4
0.24%Pt-Al_2O_3(1)	155	10	17.6	6.1	2.0
0.24%Pt-SiO_2-Al_2O_3(1)	145	21.5	31.4	7.5	2.5
0.5%Rh-Al_2O_3(0.5)	140	10	9.2	7.0	1.3
0.5%Ru-Al_2O_3(0.5)	175	10	-	2.2	0.5
0.24%Ir-Al_2O_3(1)	180	10	0	0	0

Benzene 30g, $NaCl\text{-}AlCl_3$(1:1 molar ratio) 3-4g.

A combination of Pd-Al_2O_3 and fused salts($NaCl\text{-}AlCl_3$, 1:1 molar ratio) showed an excellent conversion in the hydroalkylation of benzene at 105°C. The yield of cyclohexylbenzene reached 36.9% and bicyclohexyl as a succesively hydrogenated product of cyclohexylbenzene was 0.6% for 5 hr. Platinum, rhodium, ruthenium and iridium gave a poor yield. The effect of the chlorides in the hydroalkylation of benzene was shown in Table 2.

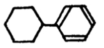
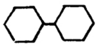
Table 2 . Effect of chlorides of fused salts in the hydroalkylation of benzene

Fused salts (g)	Temp. (°C)	Time (hr)	Yield(%)		
					
$LiCl\text{-}AlCl_3$(4)	105	5	4.0	2.5	0.5
$NaCl\text{-}AlCl_3$(2)	105	10	28.4	20.3	1.2
$KCl\text{-}AlCl_3$(2)	140	1.5	50.6	0.2	0
$CsCl\text{-}AlCl_3$(2)	180	2	67.7	0.1	0.01
$NH_4Cl\text{-}AlCl_3$(2)	140	3	49.8	0.3	0.02
$CuCl\text{-}AlCl_3$(4)	180	5	trace	0.4	0.1
$AgCl\text{-}AlCl_3$(4)	180	5	trace	0.4	0.04

Benzene 30g, 0.24%Pd-SiO_2-Al_2O_3 1.0g, fused salts(1:1 molar ratio).

AgCl and CuCl were reduced to Ag and Cu metal under the reaction condition. Furthermore, in these cases, aluminum chloride liberated from AgCl-$AlCl_3$ and CuCl-$AlCl_3$ disturbed the hydrogenation of benzene. When alkaline metal chlorides were used, the following order of activity has been obtained; NaCl, LiCl, KCl and CsCl. The relation of the reaction temperature vs. the yield of cyclohexylbenzene was shown in Table 3. Cyclohexylbenzene was observed above 80°C. The yield of cyclohexylbenzene and bicyclohexyl reached 54.7 and 5.1% at 140°C for 5 hr. At more elevated temperatures, the yield of cyclohexylbenzene decreased and cyclohexane, a hydrogenation product of benzene, increased.

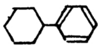
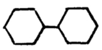
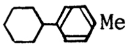
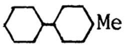
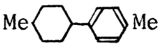
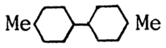
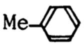
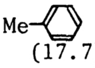
Table 3. Relation of the reaction temperature vs. the yield of cyclohexylbenzene in the hydroalkylation of benzene

Temp. (°C)	Yield(%)			
				
80	39.1	28.0	32.1	0.3
105	42.1	20.5	36.9	0.6
140	13.3	24.4	54.7	5.1
180	17.9	69.7	8.8	3.5

Benzene 30g, 0.24%Pd-Al_2O_3 1.0g, NaCl-$AlCl_3$(1:1 molar ratio) 4.0g, 5 hr.

Toluene was also hydroalkylated as shown in Table 4. In this case, 4,4'-dimethylcyclohexylbenzene and 4,4'-dimethylbicyclohexyl were obtained. When a mixture of benzene and toluene(1:1 molar ratio) was submitted to the hydroalkylation, six products were obtained.

Table 4. Hydroalkylation of benzene and toluene with Pd-Al_2O_3 and NaCl-$AlCl_3$

Compound (g)	Yield(%)					
						
 (25)	0	0	0	0	11.0	3.8
 (15) +  (17.7)	2.2	1.1	11.0	3.2	19.8	3.3

0.24%Pd-Al_2O_3 1.0g, NaCl-$AlCl_3$(1:1 molar ratio) 4.0g, 120°C, 6 hr.

In the hydroalkylation of benzene, cyclohexene has been proposed as an intermediate compound.[3),8)] In our system, the role of alkaline metal chlorides are still ambiguous. But, two possible roles are considered. One is the suppression of the solubility of aluminum chlorides to benzene in the hydrogenation on Pd-Al_2O_3 and another one is the stabilization of cyclohexene on NaCl-$AlCl_3$

under the course of alkylation. Details are being studied in our laboratory and the results will be reported elsewhere at a later date.

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