CHEMISTRY LETTERS, pp. 277-278, 1977. Published by the Chemical Society of Japan

t-BUTYLATION AND ISOPROPYLATION OF TOLUENE WITH t-BUTYL AND ISOPROPYL CHLORIDES CATALYZED BY CALCINED IRON SULFATE TREATED WITH HYDROGEN CHLORIDE

Makoto HINO* and Kazushi ARATA**
* Hakodate Technical College, Tokura-cho, Hakodate 042
**Hokkaido University of Education, Hachiman-cho, Hakodate 040

The title reaction was carried out at room temperature over catalysts prepared by calcining $FeSO_4$, Fe_2O_3 and $Fe(OH)_3$ in air at various temperatures, followed by treating with HCl. The $FeSO_4$ catalyst heat-treated at 700°C showed surprisingly high activity and selectivity, whereas other catalysts were almost inactive.

t-Butylation and isopropylation of toluene with their corresponding chlorides are known to proceed over Lewis-type catalysts such as anhydrous aluminum chloride1) and boron trifluoride.2) It was previously reported that iron sulfates calcined in air showed high catalytic activity and selectivity for the benzylation and benzoylation of toluene in comparison with those of other solid acid catalysts such as nickel sulfate and silica alumina, the maximum activity being at 700°C of calcination.3,4) We have continued further investigations of these catalytic actions and found the remarkable increase of their activity when treated with hydrogen chloride. This new catalyst was attempted to the above alkylations.

The reaction was carried out with 50 ml of 0.5 M t-butyl chloride or isopropyl chloride in toluene and weighed catalyst (0.1 g for t-butylation and 0.5 g for isopropylation) with stirring at room temperature. The reaction products separated from the catalyst were analyzed by gas chromatography using a 5 m column of tricresyl phosphate on Celite 545. The catalyst was prepared by calcining a guaranteed grade reagent of $FeSO_4 \cdot 7H_2O$, Fe_2O_3 or $Fe(OH)_3$ in air for 3 hr, followed by exposing to a stream of the mixed gas of N_2 (20 ml/min) and HCl (26 ml/min) for 20 min and finally to N_2 gas for 30 min. The prepared catalyst was stored in a sealed ampoule until use.

Both alkylations did not occur at all over $FeSO_4$ calcined at any temperature, without the HCl treatment, at room temperature. Table 1 shows % conversion of the alkylations and % yield of the products. The catalytic activity of $FeSO_4$ changed remarkably by the calcination temperature. The sulfate heat-treated at 700°C showed strikingly high avtivity. The mixture of product after the 100 % completion of the reaction was quite clear, and any products other than listed in the table were not detected. It was observed that $FeSO_4$ is decomposed to form α-Fe_2O_3 over 700°C of calcination in air.4) Thus, commercially available Fe_2O_3

Table 1. t-Butylation and isopropylation of toluene at room temperature

Catalyst		t-Butylation			Isopropylation		
	Temp. of calcn. (°C)	Conversion (%)	Reaction time (hr)	Prods.[a)] (%) o-,m-,p-	Conversion (%)	Reaction time (hr)	Prods.[b)] (%) o-, m-, p-
$FeSO_4$	500	7	3		trace	3	
	600	9	3				
	700	86	10 min	-, 5, 95	73	30 min	46, 22, 32
	700[c)]	0	24		0	24	
	800	15	20 min	-, 4, 96	2	3	
	900	5	3				
Fe_2O_3	500	< 1	3		trace	3	
	700	9	3		trace	3	
	900	< 1	3		trace	3	
$Fe(OH)_3$	700	5	3				

a) t-butyltoluene, b) isopropyltoluene, c) without treatment with HCl.

and $Fe(OH)_3$ were calcined around 700°C and treated analogously with HCl, but these catalysts were almost inactive for both reactions as shown in the table. The catalyst of the 700° treatment also produced 94 % t-butylbenzene in the t-butylation of benzene with t-butyl chloride (catalyst: 0.2 g) in 10 min and 86 % isopropylbenzene in the isopropylation of benzene with isopropyl chloride (cat.: 1.1 g) in 5 min at room temperature under the same reaction conditions.

On exposure to HCl at room temperature, $FeSO_4$ calcined at 700°C caused the violent evolution of heat in 10 min after the exposure, and the sulfate treated at 800°C did slightly. The heat seems to be related with the catalytic activity, because other materials except the sulfates treated at 700 and 800°C did not produce any heat. Even the $FeSO_4$(700°) was inactive when the HCl treatment was ceased before the generation of heat. This heat may be attributed to the formation of $FeCl_3$ on the surface. However, the activity of commercial $FeCl_3$ for the present alkylations under the same reaction conditions was much lower than the $FeSO_4$(700°) catalyst. This catalyst also showed the considerable activity for the reaction of toluene with methanesulfonyl chloride at 100°C, while $FeCl_3$ was not active.

References

1) G. A. Olah, S. H. Flood, and M. E. Moffatt, J. Am. Chem. Soc., 86, 1060 (1964).
2) R. Nakane, O. Kurihara, and A. Takematsu, J. Org. Chem., 36, 2753 (1971).
3) K. Arata, K. Sato, and I. Toyoshima, J. Catal., 42, 221 (1976).
4) K. Arata, K. Yabe, and I. Toyoshima, J. Catal., 44, 385 (1976).

(Received January 5, 1977)