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Catalytic Property of Calcined Iron Sulfate Treated with Hydrogen Chloride in Alkylation of Toluene and Benzene with Alkyl Chlorides[1]

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Alkylation was carried out at room temperature over catalysts prepared by calcination of $FeSO_4$, Fe_2O_3, and $Fe(OH)_3$ in the air at various temperatures and subsequent exposure to HCl at room temperature for 20 min. The $FeSO_4$–HCl catalysts heat-treated at 700 and 750 °C showed very high activity and selectivity, the other catalysts except for the sulfate treated at 800 °C being almost inactive. The $FeSO_4$(700 °C)–HCl catalyst was found to consist of $FeCl_3$ and α-Fe_2O_3 by means of Mössbauer effect, the absorption peak areas being 14 and 86% for portions of iron based on the chloride and oxide, respectively. The results of DTA and TGA experiments suggest that the coordinate bond of water molecule on $FeCl_3$ of the $FeSO_4$(700 °C)–HCl catalyst is stronger than that on $FeCl_3$ of the $FeSO_4$ (600, 800, and 900 °C)–HCl and commercial $FeCl_3$. The $FeSO_4$(700 °C)–HCl catalyst showed a much higher activity than pure $FeCl_3$. The iron(III) chloride formed by reaction of HCl and α-Fe_2O_3 obtained by thermal decomposition of the sulfate at 700 or 750 °C was found to be a very strong Lewis acid catalyst.

t-Butylation and isopropylation of toluene and benzene with *t*-butyl and isopropyl chlorides are generally catalyzed by Lewis acids such as anhydrous aluminum chloride[2] and boron trifluoride.[3] This type of catalyst has been mostly used for the Friedel-Crafts reaction.[4]

No data are available on the alkylation catalyzed by solid acids such as SiO_2–Al_2O_3 and metal sulfates at room temperature. We examined the reactions over heat-treated $FeSO_4$, which showed high catalytic activity and selectivity for benzylation and benzoylation of toluene with the corresponding chlorides in comparison with those of other solid acid catalysts, $NiSO_4$, SiO_2–Al_2O_3, *etc.*,[5] although the catalyst was inactive for alkylation at room temperature. However, treatment with HCl remarkably promoted catalytic activity. The $FeSO_4$ catalyst prepared by calcination in the air at a certain temperature followed by treatment with HCl was found to show exceedingly high activity, its activity being higher than that of anhydrous $FeCl_3$.

Experimental

Materials and Catalysts. Toluene and benzene (guaranteed reagents) were purified by distillation over sodium metal. *t*-Butyl and isopropyl chlorides (guaranteed reagents, Tokyo Kasei Kogyo Co.) were used without further purification. Catalysts were prepared as follows: $FeSO_4 \cdot 7H_2O$ (guaranteed reagent, Kanto Chemicals Co.), Fe_2O_3 (Wako Pure Chemical Co.) and $Fe(OH)_3$ (Kokusan Chemical Works, Ltd.) were heated at 150 °C in the air for 1 h, and powdered below 100 mesh size. They were then calcined in Pyrex or quartz glass tubing at various temperatures in the air for 3 h and kept in sealed glass tubings. Catalysts thus prepared were exposed to a stream of 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. Hydrogen chloride gas was obtained by dropping concd hydrochloric acid into concd sulfuric acid, followed by passing the gas through concd sulfuric acid twice and cooling to −72 °C three times for drying. The catalyst thus prepared was sealed in an ampoule.

Procedure for Reaction. The reaction was carried out by stirring a mixture of weighed catalyst and 50 ml of 0.5 M toluene solution of *t*-butyl or isopropyl chlorides at room temperature. At appropriate time intervals, a small amount of the sample was taken out with a 1 ml syringe, separated from the catalyst, and analyzed by gas-liquid chromatography with a TCD detector using a 5 m column of tricresyl phosphate on Celite 545 (110 °C; He, 3.0 kg/cm^2). The yields of products were estimated on the basis of unreacted chloride and calculated by measurement of GLC peak areas (corrected). The competitive *t*-butylation of benzene and toluene was carried out with 0.5 M *t*-butyl chloride in equimolar amounts of benzene and toluene.

Physical Measurements. Differential thermal analysis (DTA) and thermal gravimetrical analysis (TGA) diagram were recorded at a heating rate of 10 °C/min from room temperature to 720 °C with a Rigaku CN8002. Infrared spectra were obtained with a Hitachi EPI-G2 spectrophotometer using Nujol and KBr tablets. Mössbauer spectra were recorded on an Elron Mössbauer effect radiation analyzer, using a ^{57}Co–Cu source at room temperature. The spectrum of the 90% ^{57}Fe-enriched iron foil was used for calibration of velocity scale.

Results and Discussion

No report seems to be available concerning the Friedel-Crafts *t*-butylation and isopropylation of aromatics with *t*-butyl and isopropyl halides as the alkylation reagents catalyzed by solid acids such as Al_2O_3 and SiO_2–Al_2O_3. No alkylation of toluene with *t*-butyl and isopropyl chlorides took place at room temperature over calcined $FeSO_4$, a solid acid. However, remarkable increase in the catalytic activity of $FeSO_4$ was caused by treatment with HCl, in which $FeSO_4$ was exposed to HCl gas at room temperature for 20 min after calcination. The catalytic activity and product distribution for the reactions at room temperature over catalysts prepared by calcination of $FeSO_4$ in the air at various temperatures, followed by treatment with HCl are given in Tables 1 and 2. The catalytic activity changed markedly with the calcination temperature of $FeSO_4$. The sulfates heat-treated at 700 and 750 °C showed strikingly high activity, $FeSO_4$ (800 °C)–HCl** being also highly active for *t*-butyla-

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** This indicates a HCl-treated catalyst of $FeSO_4$ calcined at the temperature in parentheses.

TABLE 1. *t*-BUTYLATION OF TOLUENE OVER IRON SALTS TREATED WITH HYDROGEN CHLORIDE AT ROOM TEMPERATURE (catalyst : 0.1 g)

Catalyst	Temp of calcn./°C	Reaction time/h	Conversion/%	Yield of *t*-butyltoluene/%		
				ortho-	*meta-*	*para-*
$FeSO_4$-HCl	500	3	7.0			
	600	3	8.5			
	650	3	14.6			
	700	3 min	29.7			
	700	10 min	86.2	—	5.2	94.8
	750	3 min	38.5			
	750	10 min	100.0	—	5.8	94.1
	800	20 min	14.6	—	4.1	95.9
	900	3	5.2			
$FeSO_4$[a]	700	24	0			
Fe_2O_3-HCl	500	3	0.5			
	700	3	9.4			
	900	3	0.5			
$Fe(OH)_3$-HCl	700	3	5.3			

a) No treatment with HCl.

TABLE 2. ISOPROPYLATION OF TOLUENE OVER IRON SALTS TREATED WITH HYDROGEN CHLORIDE AT ROOM TEMPERATURE (catalyst : 0.5 g)

Catalyst	Temp of calcn./°C	Reaction time/h	Conversion/%	Yield of *i*-propyltoluene/%		
				ortho-	*meta-*	*para-*
$FeSO_4$-HCl	500	3	trace			
	700	10 min	6.3			
	700	30 min	73.1	45.7	21.7	32.6
	750	10 min	8.0			
	750	30 min	98.6	43.5	22.7	33.8
	800	3	1.7			
$FeSO_4$[a]	700	24	0			
Fe_2O_3-HCl	500	3	trace			
	700	3	trace			
	900	3	trace			

a) No treatment with HCl.

tion. Figure 1 shows the time course of both reactions over these catalysts. In the case of *t*-butylation over $FeSO_4$ (700 °C and 750 °C)–HCl, the progress of reaction was linear with time up to over 50% completion, the reaction afterwards following first-order kinetics with respect to the *t*-butyl chloride concentration. Some of the reactions showed S-shaped curves, probably owing to the promotion effect of HCl formed by the reaction.

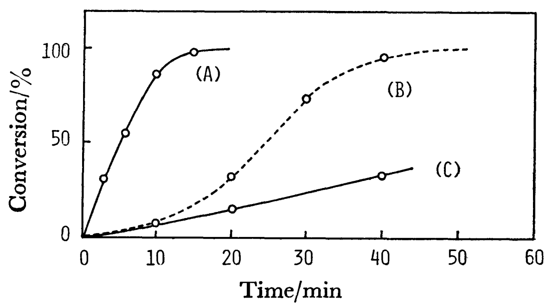

Fig. 1. *t*-Butylation and isopropylation of toluene over $FeSO_4$ treated with HCl at room temperature. *t*-Butylation (——), isopropylation (---). Heat-treatment of $FeSO_4$: 700 °C for (A) and (B); 800 °C for (C). Catalyst amount: 0.1 g for (A) and (C); 0.5 g for (B).

The reaction mixture after the 100% completion of the reaction was quite clear, no products other than listed in the Tables being detected. The isomer distributions of *t*-butyltoluenes and isopropyltoluenes did not change at 0 °C reaction temperature and were also the same as those observed for the general Friedel-Crafts Lewis catalysts such as $AlCl_3$[2] and BF_3.[3]

The activity of $FeSO_4$–HCl is low at 650 °C calcination as compared with the remarkable activity at 700 °C treatment. $FeSO_4$ decomposes completely to form α-Fe_2O_3 at temperatures in the range 675—700 °C, crystallization proceeding rapidly afterwards.[6] Commercially available Fe_2O_3 and $Fe(OH)_3$ were calcined around 700 °C and treated with HCl, but the catalysts were almost inactive for both reactions (Tables 1 and 2).

The present catalysts were examined in the *t*-butylation and isopropylation of benzene with *t*-butyl and isopropyl chlorides at room temperature under the same reaction conditions, the following results being obtained: $\mathrm{FeSO_4}$ (700 °C)–HCl and $\mathrm{FeSO_4}$(800 °C)–HCl gave 94.3% *t*-butylbenzene in 10 min and 84.6% in 30 min, respectively, 85.5% isopropylbenzene being produced by $\mathrm{FeSO_4}$(700 °C)–HCl in 5 min.7) The sulfates–HCl heat-treated at 500, 600, and 900 °C showed conversion below 4% for *t*-butylation and isopropylation.

When a large amount of $\mathrm{FeSO_4}$(700 °C)–HCl was used for *t*-butylation of toluene, isomerization of *t*-butyltoluene took place; *i.e.* isomerization from the *para*- to the *meta*-position up to the equilibrium composition of 64% *m*- and 36% *p*-*t*-butyltoluene.2) The reaction with 1.0 g catalyst at room temperature gave 23.9% *m*- and 76.1% *p*-isomer at 5 min, 40.4 and 59.6 at 15 min, and 61.5 and 38.5 at 60 min, respectively. No isomerization was observed even over a period of 3 h when the catalyst amount was 0.1 g.

The competitive *t*-butylation of benzene and toluene at room temperature was carried out with 0.5 g of the above catalyst in equimolar amount. The secondary reactions such as transalkylation between *t*-butyltoluene and benzene and the isomerization of *t*-butyltoluene took place. The apparent $k_\mathrm{T}/k_\mathrm{B}$ value (the relative rate of toluene to benzene, estimated from yields of *t*-butyltoluene and *t*-butylbenzene) decreased with time as was observed by Shimada.8) The $k_\mathrm{T}/k_\mathrm{B}$ value obtained was 14.7 at 1 min, 8.7 at 3 min, 4.8 at 10 min, and 1.5 at 60 min. The isomer distribution of *t*-butyltoluene was 6.6% *m*- and 93.4% *p*-form at 1 min and 52.7% *m*- and 47.3% *p*-form at 60 min.

On exposure to HCl at room temperature, the sulfates calcined at 700 and 750 °C evolved heat violently in 10 min, but $\mathrm{FeSO_4}$ treated at 800 °C only slightly. The heat evolution seems to be related with the catalytic activity, since other materials except for the sulfates treated at 700, 750, and 800 °C evolved no heat. Even the $\mathrm{FeSO_4}$(700 °C)–HCl was inactive when HCl treatment was stopped before heat generation. Figure 2 shows the catalytic activity of $\mathrm{FeSO_4}$ (700 °C) with various periods of the HCl treatment for the isopropylation of benzene. The activity increases with duration of the treatment after the beginning of heat generation. The catalyst before the generation of heat was extremely low in activity even for the *t*-butylation of toluene, an easier reaction than isopropylation, though its activity was still high in comparison with that without any HCl treatment (Tables 1 and 2).

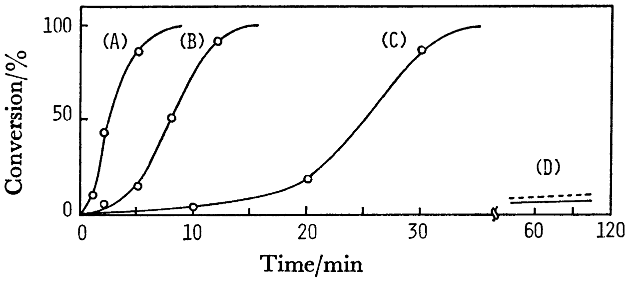

Fig. 2. Catalytic activity of $\mathrm{FeSO_4}$ (700 °C) with different periods of the HCl treatment for the isopropylation of benzene at room temperature (catalyst: 1.1 g). The HCl treatment was ceased 10 min (A), 1 min (B), at once (C) after beginning of the heat generation and before (D) the generation. (---): *t*-butylation of toluene (catalyst: 0.1 g).

Heat generation by HCl treatment is considered to be due to the formation of $\mathrm{FeCl_3}$ on the surface. In order to confirm the existence of $\mathrm{FeCl_3}$, Mössbauer experiment on $\mathrm{FeSO_4}$(700 °C)–HCl was carried out. The spectrum obtained is shown in Fig. 3. The spectrum consists of a single peak around zero velocity and other six peaks showing magnetic hyperfine splitting. The single peak is attributed to $\mathrm{FeCl_3}$, the isomer shift 0.45±0.05 mm/s being close to 0.37 mm/s for commercial $\mathrm{FeCl_3}$ and 0.36 mm/s for the value obtained by DeBenedetti *et al.*9) The other six lines are attributed to α-$\mathrm{Fe_2O_3}$,5) indicating that $\mathrm{FeSO_4}$ is decomposed to form $\mathrm{Fe_2O_3}$ at 700 °C calcination. From absorption peak areas, the portions of iron based on $\mathrm{FeCl_3}$ and α-$\mathrm{Fe_2O_3}$ were found to be 14 and 86%, respectively.

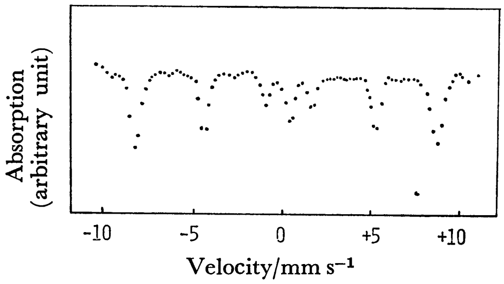

Fig. 3. Mössbauer spectrum of $\mathrm{FeSO_4}$ (700 °C)–HCl. Isomer shift referred to metallic iron.

IR spectrum of $\mathrm{FeSO_4}$(700 °C)–HCl showed an absorption band at 1600 cm^{-1}, which is assigned to a water molecule coordinated to $\mathrm{FeCl_3}$.10) The intensity of the band decreased when the substance was dried in the air at 150 °C for 2 h. The catalytic activity of the dried catalyst was higher than that of $\mathrm{FeSO_4}$ (700 °C)–HCl, not subjected to drying, *viz.*, conversion for *t*-butylation of toluene at room temperature was 34.2% at 3 min, and 100% at 10 min (*cf.* Table 1).11)

DTA and TGA of the catalysts were measured as shown in Fig. 4. The endothermic peaks appearing at 130—160 °C in all the samples are ascribed to the desorption of water molecule bonded coordinately to $\mathrm{FeCl_3}$ formed by HCl treatment. A similar peak was observed around 140 °C in the case of pure anhydrous $\mathrm{FeCl_3}$, a corresponding sharp decrease in weight being observed. Endothermic desorption of the water molecules is observed at much higher temperature, 160 °C for $\mathrm{FeSO_4}$(700 °C)–HCl, and at a slightly higher one, 144 °C, for $\mathrm{FeSO_4}$(800 °C)–HCl than that for other materials treated at 600 and 900 °C. The difference in temperature is connected with their catalytic activities (Table 1). The activity of the $\mathrm{FeSO_4}$(700 °C)–HCl catalyst was much higher than that of anhydrous $\mathrm{FeCl_3}$ (guaranteed reagent, Wako Pure Chemical Co.) for isopropylation, the activity

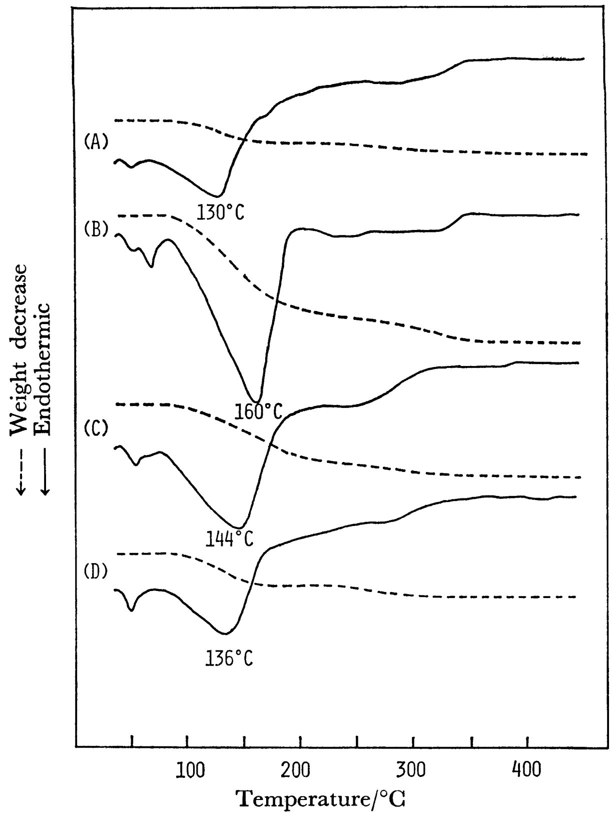

Fig. 4. DTA (——) and TGA (---) curves of $FeSO_4$ heat-treated at various temperatures, followed by treating with HCl. (A): 600 °C (21.7 mg), (B): 700 °C (25.3 mg), (C): 800 °C (30.0 mg), (D): 900 °C (30.0 mg).

ratio being greater than 10. The former also showed marked activity for the reaction of toluene with methanesulfonyl chloride at 100 °C, but not $FeCl_3$. It seems that the high temperature of desorption of water is based on the strong coordinate bond between water and the surface $FeCl_3$. Thus, the iron(III) chloride formed by reaction of HCl and α-Fe_2O_3, prepared by the thermal decomposition of the sulfate at 700 or 750 °C, could be a quite strong Lewis acid catalyst.

Gradual decrease in weight was observed in the temperature range 200—350 °C. This seems to be due to the sublimation of $FeCl_3$. The weight decrease was estimated as 1.6, 7.8, 3.5, and 2.0% for the 600, 700, 800, and 900 °C catalysts, respectively (adsorbed water observed up to 200 °C in TGA was not included in calculation).

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11) The catalysts dried at 250 and 350 °C gave 21.7% conversion at 2.5 h and 17.2% at 3 h, respectively. The cause of low activities might be due to the sublimation of $FeCl_3$ on the surface, since some black-colored substance, seemingly $FeCl_3$, was observed on the upper wall of a test tube used for drying.