Catalytic Activity of Iron Sulfates for Friedel–Crafts Type Benzylation of Toluene with Benzyl Chloride

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Ferrous and ferric sulfates prepared by calcining their hydrates in air from 200 to 700°C showed surprisingly high catalytic activity and selectivity for the title reaction. The activities observed at 45 and 53.5°C showed the higher calcination temperature, the higher catalytic activity, and the shorter induction period. Ferrous sulfate heat treated at 500°C *in vacuo* showed the maximum activity. The activation energies over $FeSO_4$, calcined at 400 and 600°C were quite small, 2.7 and 5.1 kcal mol^{-1}, respectively. The products were 42% *ortho*-, 6% *meta*-, and 51% *para*-benzyltoluene with an almost negligible amount of polymer in all the analyzed runs. The ratios of rates in toluene and benzene, k_T/k_B, were 6.29 and 6.60 for $FeSO_4$ and $Fe_2(SO_4)_3$ calcined at 700°C, respectively. From these values, the positional reactivities of toluene, o_f, m_f, and p_f were obtained as 9, 1, and 20, respectively. Hammett's constant, ρ, was also estimated to be $-4 \sim -5$. From these observations, the high catalytic activity and selectivity were tentatively explained by a concept that the catalyst surface deformed by complicated interactions with sulfur remained slightly on the oxide upon the decomposition of sulfate salts, and adsorbed HCl acted catalytically as a push–pull to the reactant.

INTRODUCTION

Benzylation of toluene with benzyl chloride, which is a typical example of Friedel–Crafts alkylations, is generally known to proceed over Lewis-type catalysts such as anhydrous aluminum chloride (*1*) and gallium bromide (*2*). This type of catalyst has been mostly used for the Friedel–Crafts reaction, which is one of the most studied of organic reactions (*3*).

It was also found that the benzylation proceeds over calcined nickel sulfate as a solid acid catalyst (*4, 5*). We have further examined the catalytic activity and selectivity for the reaction over other solid acids, such as alumina and calcined sulfate salts

of Fe, Zn, Co, Mn, and Cu. It was found that ferrous sulfate showed an unexpected effectiveness for the reaction. The activity was more than 100 times as large as those of the other catalysts, whereas the selectivity of these catalysts was the same (*6*). This outstanding activity of ferrous sulfate was briefly explained by Fe^{3+} supposedly being formed by calcination on the catalyst surface and acting as a Lewis-type catalyst such as $FeCl_3$ because of the much lower oxidation potential of Fe^{2+} compared to those of other metal ions.

Recently, Hasegawa and Kawaguchi have examined the surface property of ferric sulfate calcined in air by the adsorp-

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tion of 1, 1-diphenyl-2-picryl-hydrazyl (7), and Toyoshima *et al.* have also studied the structure of acidic sites of ferric and ferrous sulfates calcined in air as well as *in vacuo* for the latter by using Mössbauer spectroscopy, infrared, and X-ray in addition to the amine titration method (8).

The present study was undertaken to examine the activity and selectivity of both ferrous and ferric sulfates for the reaction of toluene with benzyl chloride, and the catalytic action of iron sulfates is discussed on the basis of the observed results.

EXPERIMENTAL

Materials and catalysts. Benzyl chloride, a guaranteed reagent of Wako Pure Chemical Co., was fractionally distilled at reduced pressure. Toluene, a guaranteed reagent, was distilled over sodium metal.

Catalysts were prepared as follows: Iron sulfates ($FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$; guaranteed reagents of Kanto Chemicals Co.) were heated at 150°C for 1 hr and powdered to 100–200 mesh and then calcined in glass tubes at various temperatures, ranging from 200 to 700°C for 3 hr in air. Ferrous sulfate was also heat treated *in vacuo*, and the prepared catalyst was immersed in 1–2 ml of toluene in a vacuum line and sealed in an ampoule until use.

Procedure and analysis of products. The rate of the benzylation reaction was determined by the amount of HCl evolved at temperatures ranging from 34.5 to 53.5°C. In a 500-ml, three-necked flask with a stopper, a nitrogen inlet, and an efficient spiral condenser, fitted with an HCl gas outlet connected to a titration assembly, was placed 50 ml of 0.5 M benzyl chloride in toluene and 0.3 g (0.15 g when calcined at 700°C) of the accurately weighed catalyst (the catalyst prepared *in vacuo* was filtered off, dried, and weighed after the reaction was completed). The HCl gas evolved was delivered by N_2 gas (3 ml/sec) into a vessel containing 100 ml of water, equipped with a pH electrode and a syringe

burette, connected to an automatic titrator (Auto Buret with pH Stat HS-1B and Polyrecorder EPR-3T, Toa Electronics Ltd.) with an alkali solution.

The flask was immersed in an oil bath with mechanical stirrer and kept at the reation temperature. After the completion of the reaction, the solvent was evaporated and the residue was distilled under reduced pressure to remove a small amount of polymer. The products were then analyzed and identified by glc comparison with the authentic samples, using a 45-m capillary column of Ucon LB-550-X (105°C; N_2, 2.0 kg/cm^2; FID detector).

RESULTS AND DISCUSSION

In the present work, the reaction temperatures were taken about 50°C lower than that in the previous experiment (6), because of the much higher activity of the present catalysts. Figure 1 shows a typical pH Stat record. HCl evolution was linear with time, after a period of induction, up to over 50% completion, and afterwards the reaction followed first-order kinetics with respect to the benzyl chloride concentration. Some of the catalysts gave S-shaped curves including the induction periods.

Figure 2 shows the initial rate and induction period of ferrous sulfate versus various calcination temperatures. It can be seen that the higher the calcination temperature, the higher the catalytic activity and the
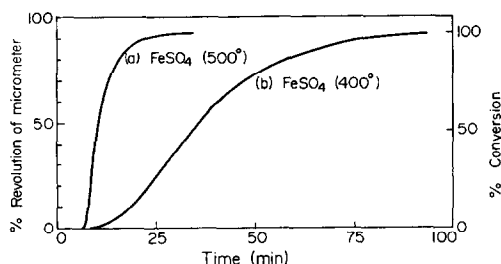

FIG. 1. Consumption of NaOH vs time recorded by a pH Stat. Reaction temperature, 45°C. Catalyst: (a), 0.306; (b), 0.266 g. Figures in parentheses show the calcination temperatures.

shorter the induction period. We also see that the induction period is inclined to be longer with the lower reaction temperature. It should be noted that the observed rates, over alumina and sulfates of Co, Mn, Ni, and Cu calcined at 350°C, were below 0.019 mol/1·min·g at 100°C (6), which was extremely small compared to the rates obtained by ferrous sulfate at 45.0 and 53.5°C or even at 34.5°C. The reaction was completed up to 80% in 2 min at 53.5°C over the catalyst calcined at 700°C. The activation energies over $FeSO_4$ calcined at 400 and 600°C were quite small, 2.7 and 5.1 kcal/mol, respectively.

The ferric sulfate catalysts were not active at all until 400°C calcination temperature. However, the activity rapidly increased with increasing of calcination temperature from 500 to 700°C. The sample calcined at 700°C shows higher activity than ferrous sulfate calcined at the same temperature with a shorter period of induction in comparison with that of ferrous sulfate (Fig. 3).

From Figs. 2 and 3, the activities are not entirely related to the acidities in the range of $pK_a = -3.0 \sim 4.8$ measured by the n-butylamine titration method, whose maxima appeared around 200 and 150°C for

Fig. 3. Catalytic activity and induction period of ferric sulfate versus calcination temperature, at 53.5°C. *, Small inset shows the acidity (butylamine titer, millimoles per gram) at $pK_a = -3.0$. See Ref. (8).

ferrous and ferric sulfates, respectively (8). Hasegawa and Kawaguchi also observed the maximum acidity of ferric sulfate when calcined at 120°C, and its amount was about 10 times as much as that of other sulfates such as Al, Mg, and Ni (7). As is well known, the Friedel–Crafts reaction is catalyzed by acid sites over a Lewis catalyst and the sites must be strong enough to make a halogen compound polarize or ionize. Therefore, this benzylation seems to be far from a usual acid-catalyzed reaction. Thus, the present catalysts formed from the sulfate by calcining at high temperature have a different nature from the usual Lewis catalysts.

The reaction rates were also not directly related to the acidities of the other sulfate catalysts and rather proportional to BET surface area in the case of nickel sulfate (4, 6). The explanation of the induction period and apparent lack of correlation of the rate with acidities of the catalyst in the previous paper were as follows: The function of the intrinsic acidic sites on the catalyst was only in initiating the reaction, then the initially formed HCl on the catalyst remained adsorbed on the surface, and finally adsorbed HCl, in turn, acted as a
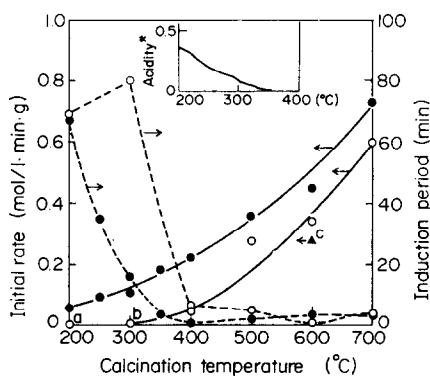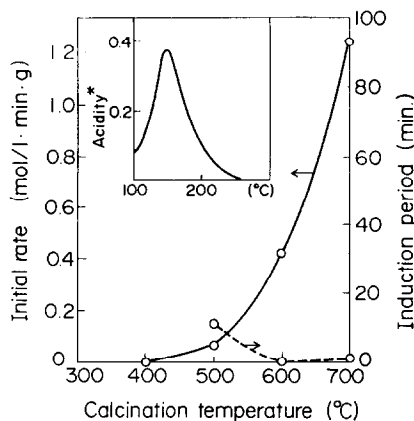

Fig. 2. Catalytic activity and induction period of ferrous sulfate versus calcination temperature at 45.0 and 53.5°C, (a), 0.0024; (b),0.0043 mol/1·min·g; (c), at 34.5°C with 13-min induction period. *, Small inset shows the acidity (butylamine titer, millimoles per gram) at pK_a 1.5. See Ref. (8).

true catalyst. This model is not particularly attractive in explaining the outstanding activity of iron sulfates, because it is hard to say that the heat-treated iron sulfate has a surface area more than 100 times as large as that of other sulfates such as those of Zn, Co, and Ni. In fact, the BET surface area of ferrous sulfate calcined at 700°C was 63 m²/g. SiO₂-Al₂O₃, which has quite strong acid sites and large surface area, was not active at all for 2 hr under the mild reaction conditions used in the present work (9).

Iron sulfate is dehydrated to produce the anhydrous form above 200°C and then decomposed to form the iron oxide above 500°C (10, 11). The decomposition of iron sulfates at 700°C to their oxides was experimentally shown from weight loss (12). Therefore, the activity upon the present reaction of Fe₂O₃ calcined at 700°C was examined. The rate over this catalyst was 40 times as small as that of Fe₂(SO₄)₃ calcined at the same temperature. The differently prepared ferric oxide catalyst, where ferric hydroxide (Kokusan Chemical Works, Ltd.) was calcined at 700°C in air, was also inactive at all at 53.5°C for 3 hr. However, the sulfur-treated ferric oxide, which was prepared by exposing ferric oxide (prepared from the hydroxide) to H₂S at room temperature for 45 min and then calcining at 500°C for 1.5 hr, showed 0.065 mol/l·min·g as a rate after 23 min of induction. From these observations, it can be said that this reaction is not catalyzed by the oxide surface, whereas the slight amount of sulfur remaining on the oxide upon the decomposition of sulfate salts is catalytically significant. Takeuchi et al. have recently observed that sulfurated nickel was catalytically inactive for the hydrogenation of olefin but active for the isomerization of butene and the C₂H₄–C₂D₄ exchange reaction in coexistence with hydrogen and that, on contact with acetylene, the surface becomes active for the hydrogenation of olefin and the H₂–D₂ equi-
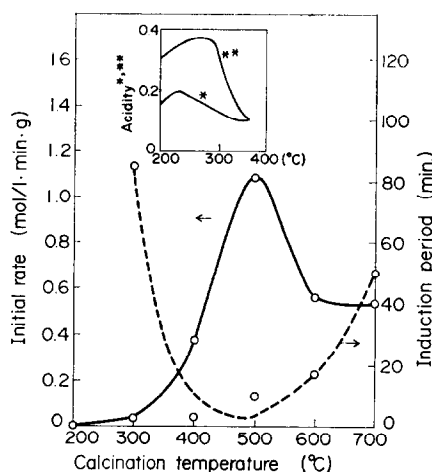

FIG. 4. Catalytic activity and induction period of ferrous sulfate calcined *in vacuo* versus calcination temperature at 53.5°C *, **. Small inset shows the acidity (butylamine titer, millimoles per gram) at $pK_a = 1.5^*$ and 4.8**. See Ref. (8).

librium as well as the hydrogenation of acetylene (13, 14). Accordingly, it might be concluded that slightly sulfurated iron oxides were quite active in coexistence with hydrogen chloride.

Figure 4 shows the catalytic activity and induction period of ferrous sulfate calcined *in vacuo*. The maximum activity was shown over the catalyst calcined at 500°C, but less reproducibility was observed in the case of the vacuum-treated catalyst, especially one calcined at 500°C. The catalyst was filtered off, dried, and weighed at the end of the reaction, and then the rate per gram was not so precise. The induction period was much longer than that of the air-treated catalyst when calcined at 600 and 700°C, indicating that the relationship between the activity and induction period is somewhat complicated. The apparent movement of calcination temperature, at which the activity is maximum, is supposed to be due to the elimination of sulfur from the catalyst *in vacuo*.

The product distribution in all the analyzed runs was almost the same with the negligible amount of polymer, as shown in Table 1. This similarity of the product

TABLE 1

Isomer Distribution in the Iron Sulfate-Catalyzed
Benzylation of Toluene at 53.5°C

Catalyst	Calcination temperature (°C)	Benzyltoluene (%)		
		Ortho-	Meta-	Para-
FeSO$_4$	400[a]	42.9	5.9	51.2
	400[b]	42.2	7.0	50.8
	600	42.6	6.6	50.8
	400[c]	42.1	6.3	51.6
	500[c]	45.0	6.4	48.6
	600[c]	41.2	7.2	51.6
Fe$_2$(SO$_4$)$_3$	500	42.4	6.5	51.1
	600	42.0	6.4	51.6
	700	42.6	6.4	51.1

[a,b] The reaction was carried out at 30.7 (a) and 100°C (b).

[c] The catalysts were calcined in vacuo.

distribution implies that the catalytic actions upon this benzylation are not different; that is, the catalytic actions are independent of ferrous or ferric sulfate, reaction temperature, reaction rate, calcination temperature, and calcination in air or in vacuo.

In the alkylation of the usual Friedel–Crafts reaction, the rate-determining step

is shown to be the π-complex formation by Olah (15) and the σ-complex formation by Brown (16), and the relationship between the k_T/k_B (the ratio of rate in toluene and benzene) value and the amount of meta-isomer are different in both cases (see Table 2). Recently, Nakane studied the intermediate species of the Friedel–Crafts alkylation in detail (17) and found it to be the oriented π-complex by alkyl carbonium ion, a strong electrophile, in nonpolar solvents such as n-hexane and cyclohexane and to be, on the other hand, the termolecular-oriented π-complex, a mild electrophile, in polar solvents such as nitromethane, and the rate-controlling step was concluded to be the σ-complex formation from these π-complexes (18). From their results, the relative rate, k_T/k_B, was small for the former case (see Table 2).

Although these observations were obtained in the homogeneous system, it may be quite interesting to apply this concept to our heterogeneous system. In the present investigation, k_T/k_B values were 6.29 and 6.60 for FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ calcined at 700°C (19), respectively, and very close to that of NiSO$_4$. The large values of partial rate factors, o_f, m_f, p_f, indicate the mild-

TABLE 2

Partial Rate Factors of Toluene with Benzyl Chloride

Catalyst	Solvent	k_T/k_B	Isomer ratio (%)			Partial rate factors			Reference
			Ortho-	Meta-	Para-	o_f	m_f	p_f	
BF$_3$	C$_6$H$_{12}$	0.68	45.3	4.5	50.2	0.93	0.09	2.05	Nakane[a]
BF$_3$	n-C$_6$H$_{14}$	0.70	45.4	4.8	49.8	0.96	0.12	2.10	Nakane[a]
BF$_3$	CH$_3$NO$_2$	2.83	43.7	6.7	49.6	3.71	0.57	8.42	Nakane[a]
AlCl$_3$	CH$_3$NO$_2$	3.20	43.5	4.5	52.0	4.2	0.43	10.0	Olah[b]
GaBr$_3$	CH$_3$NO$_2$	4.0	41.1	19.4	39.5	4.9	2.3	9.4	Brown[c]
NiSO$_4$ (250°C)	Toluene	8.2	45.4	7.8	47.0	11.2	1.30	23.2	Author[d]
FeSO$_4$ (700°C)	Toluene	6.29	40.9	6.5	52.6	9.93	1.23	19.85	Author[e]
Fe$_2$(SO$_4$)$_3$ (700°C)	Toluene	6.60	42.6	6.4	51.1	8.43	1.27	20.24	Author[e]

[a] See Ref. (17).

[b] See Ref. (15).

[c] See Ref. (16).

[d] See Ref. (6).

[e] Present report.

ness of polarization caused by the catalyst or the large electronic effect of substrate, benzene or toluene, which implies the possibility of the mild electrophile.

In order to know the raction mechanism in detail Hammett's constant, ρ, was also estimated from Brown's relationship between ρ and log p_f to be $-4 \sim -5$, which was similar to that of $NiSO_4$. This fact indicates that push of a reactant to the electrophilic species, $C_6H_5{}^{+\delta} CH_2-\overset{..}{C}\overset{..}{l}$: (Cat$^{-\delta}$), is comparatively large. Consequently, this benzylation reaction is supposed to proceed on the push–pull mechanism as follows.

Catalyst
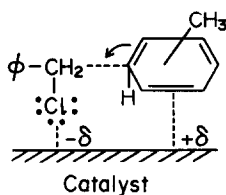
It is quite interesting that nickel sulfate and iron sulfates gave the same substrate (k_T/k_B) and positional (o_f, m_f, p_f) selectivities, supposedly indicating the same mechanism, while the activity of iron sulfates was several hundred times as large as that of nickel sulfate. On the present catalysts, the push–pull effect was probably strong. In other words those catalysts have a sort of bifunctional action to give push–pull to the reactant. The catalyst surface deformed by the complicated interactions with ion, O, S, and adsorbed HCl must act as the catalytic push–pull effect to the reactant. However, detailed study on this subject must await further investigations.

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19. The competitive benzylation of benzene and toluene at 53.5°C was carried out with 0.5 M benzyl chloride in equimolar amount. The products were analyzed by glc using a 2-m column of PEG 1000 on Flusin T (150°C; N₂, 1.2 kg/cm² ; FID detector).