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# Friedel–Crafts Reaction in the Heterogeneous System

## V. Friedel–Crafts Benzylation and Benzoylation of Toluene Catalyzed by Calcined Iron Sulfates

KAZUSHI ARATA, KATSUMASA YABE[1] AND ISAMU TOYOSHIMA[2]

*Hokkaido University of Education, Hachiman-cho 1-2, Hakodate, Japan*

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The Friedel–Crafts benzylation of toluene with benzyl chloride was carried out at 45°C over ferrous and ferric sulfates calcined in air at 700, 800, and 900°C. The benzoylation of toluene with benzoyl chloride was also performed at 110°C over both iron sulfates heat-treated at 500, 700, 900°C. The catalysts prepared by calcining both sulfates at 700°C showed the maximum activity in both reactions. The products were 41% *ortho*-, 7% *meta*-, and 52% *para*-benzyltoluene for the benzylation and 18–22% *ortho*-, 2–4% *meta*-, and 74–78% *para*-methylbenzophenone for the benzoylation in all the analyzed runs. The ratio of rate of the benzoylation in toluene and benzene, $k_T/k_B$, was 7.4 and 6.3 for $FeSO_4$ and $Fe_2(SO_4)_3$ calcined at 700°C, respectively, which are surprisingly small compared with that for $AlCl_3$ ($k_T/k_B = 110$–$115$). From the former values, the positional selectivities of toluene, $o_f$, $m_f$, $p_f$, were obtained as 3–5, 0.4–0.9, and 32, respectively. The specific surface areas of calcined sulfates were 49–71 $m^2/g$, indicating no relationship between them and the catalytic activities. The analysis of Fe and S contents of the catalysts showed that both ferrous and ferric sulfates are mainly remained as sulfate forms at 500°C of calcination and decomposed to form iron oxides containing 0.15% S at 700°C. Mössbauer spectra showed that ferrous sulfate calcined in air consists of 73% $Fe^{2+}$ and 27% $Fe^{3+}$ at 300°C and 100% $Fe^{3+}$ above 500°C. On the basis of the observed results, the nature of active sites of catalyst was discussed.

## INTRODUCTION

In the previous paper (*1a*), the benzylation of toluene with benzyl chloride, which is an alkylation, one of the important fields of the Friedel–Crafts reaction, catalyzed by iron sulfates was reported. Ferrous and ferric sulfates prepared by calcining their hydrates in air from 200 to 700°C showed surprisingly high catalytic activity and selectivity, compared with those of other solid acids such as alumina and calcined sulfate salts of Zn, Co, Mn, and Cu. It was shown that the higher the calcination temperature, the higher the catalytic activity and the shorter the induction period. The activities were also not related to the acidities measured by the *n*-butylamine titration method. The product distributions, however, in all the analyzed runs were almost the same with the negligible amount of polymer. The high catalytic activity and selectivity over the catalyst prepared by calcining at 700°C 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 reactants.

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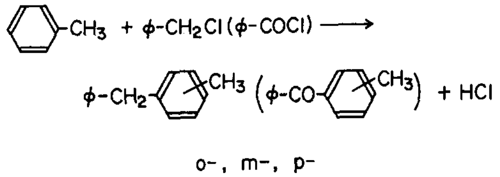
[1] Government Industrial Development Laboratory, Sapporo, Japan.

[2] Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

In order to elucidate the catalytic action of calcined iron sulfates for the Friedel–Crafts reaction, the benzylation has now been attempted over the iron sulfates calcined above 700°C. The catalysts were also applied to the benzoylation of toluene with benzoyl chloride which is an example of acylation, another important field of the Friedel–Crafts reactions. In addition to these reaction studies, analytical and physical studies were also performed to obtain informations about the properties of catalysts.



## EXPERIMENTAL

### *Materials and Catalysts*

Purification of benzyl chloride, benzoyl chloride, and toluene, and preparation of catalyst were performed as described previously (*1a*).

### *Procedure for Reaction*

The benzylation and benzoylation reactions were carried out with 50 ml of 0.5 *M* corresponding chlorides in toluene and accurately weighed iron sulfate, and their reaction rate was determined by amount of evolved HCl which was delivered by $N_2$ gas into water and titrated automatically.

The apparatus and experimental techniques in details were identical to those described previously (*1a*) with the following exceptions: the amount of catalyst was 0.04–0.07 g for the benzylation and 0.4–0.6 g for the benzoylation reaction.

The competitive benzoylation of benzene and toluene was carried out with 0.5 *M* benzoyl chloride in the equimolar amounts of benzene and toluene at 80°C. The products were analyzed by gas chromatography using a 2-m column of PEG 1000 on Flusin T (150°C; $N_2$, 2.0 kg/cm$^2$; FID).

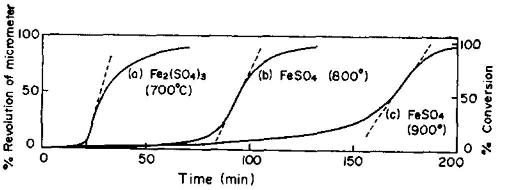


FIG. 1. Consumption of NaOH vs time recorded by a pH stat for benzylation. Reaction temperature: 45°C. Catalyst: (a) 0.046, (b) 0.048, (c) 0.064 g. (a), (b): Including induction periods, (c); after induction period was ceased. Dotted line is for estimation of activity.

*Ortho-* and *meta*-methylbenzophenone were synthesized by the reaction of the respective toluoyl chloride (Tokyo Kasei Kogyo Co., Ltd.) with benzene at 80°C over $FeSO_4$ calcined at 700°C. *Para*-methylbenzophenone was obtained from a commercial source. These three isomeric materials were used as the reference samples of the gas chromatographic analysis of the reaction products for the benzoylation, using a 45-m capillary column of Ucon LB-550-X (135°C; $N_2$, 3.0 kg/cm$^2$; FID).

Surface area of the catalyst was measured with nitrogen by the BET method. The areas obtained are shown in Table 4.

Mössbauer spectra were recorded on an Elron Mössbauer effect radiation analyzer, using a $^{57}$Co–Cu source at room temperature. Absorbers in powder form were packed in a brass holder with cellophane windows. The thickness of the absorbers was about Fe 20 mg/cm$^2$. The spectrum of the 90% $^{57}$Fe-enriched iron foil was used for calibration of velocity scale, after each measurement.

## RESULTS AND DISCUSSION

In the benzylation reaction, the reaction was performed at 45°C, that is the same temperature as that in the previous experiment (*1a*), but a smaller amount (0.04–0.07 g) of catalyst was used because of the much high activity. Figure 1 shows the time

TABLE 1

Catalytic Activity and Selectivity for Benzylation of Toluene with Benzyl Chloride at 45°C

| Catalyst | Calcination temperature (°C) | Induction period (min) | Initial rate (mol/ l·min·g) | Benzyltoluene (%) | | |
|---|---|---|---|---|---|---|
| | | | | *ortho-* | *meta-* | *para-* |
| $FeSO_4$ | 700 | 4 | 0.69 | 40.9 | 6.5 | 52.6 |
| | 800 | 31 | 0.55 | 41.5 | 7.8 | 50.7 |
| | 900 | 79 | 0.21 | 40.8 | 6.9 | 52.3 |
| $Fe_2(SO_4)_3$ | 700 | 7 | 0.74 | | | |
| | 800 | 55 | 0.19 | 40.9 | 7.1 | 52.0 |
| | 900 | 9 | 0.16 | 38.3 | 6.9 | 54.8 |

course of reaction over the catalysts heat-treated at various calcination temperatures. As shown in Fig. 1, the present catalysts gave S-shaped curves with induction periods, and it can be seen that the higher the calcination temperature, the longer the induction period and also the longer the time to complete the reaction.

Table 1 shows the catalytic activity and selectivity for the benzylation of toluene with benzyl chloride at 45°C over ferrous and ferric sulfates heat-treated at 700, 800, and 900°C. The activity, zero-order rate constant, was determined from a linear part of the curve as shown by a dotted line in Fig. 1. The catalyst prepared by heat-treating at 700°C showed the maximum activity in both ferrous and ferric sulfates. Thus, together with our previous studies, it is concluded that the catalyst calcined in air at 700°C shows the highest activity for the benzylation in the case of iron sulfates. Ferric sulfate calcined at 900°C gave a much shorter induction period than that expected from other catalysts in Table 1, but the shape of the curve in the time course of reaction was quite similar to that of $FeSO_4$ (900°C) after the induction period was ceased.

The product distributions in all the analyzed runs (Table 1), together with those over the sulfates heat-treated below 700°C in the previous paper, were quite the same. This fact implies that the catalytic actions upon this benzylation are not different over all the studied catalysts. The isomerization reaction between three isomers generally occurs with ease when catalyzed by Lewis catalysts such as $AlCl_3$ or $BF_3$. However, the isomerization is not supposed to be taking place over the present catalysts, judging from the isomer distribution; i.e., the amount of *meta*-isomer is quite small. The isomerization is usually expected to proceed from the *ortho*- to the *meta*-position or from the *para*- to the *meta*-position, on the basis of the following experimental facts: (i) the equilibrium distribution of xylene is *o*-/*m*-/*p*- = 18/60/22, and the ethylation of toluene with ethylene over $AlCl_3$ showed *o*-/*m*-/*p*- = 11/64/25 in the product distribution at 80°C, which is close to the equilibrium ratio (*2*); and (ii) the equilibrium mixture of di-*t*-butyl benzene obtained by starting from any of the three isomers over $AlCl_3$ at room temperature contained about 52% *m*- and 48% *p*-di-*t*-butylbenzene (*3*).

Since the maximum of activity was observed at 700°C of calcination in the benzylation, the catalysts treated around 700°C were attempted to the benzoylation of toluene with benzoyl chloride, which is an example of the Friedel–Crafts acylations. Figure 2 shows the time-course of reaction, and the catalytic activity and selectivity of ferrous and ferric sulfates heat-treated at 500, 700, and 900°C are summarized in

TABLE 2

Catalytic Activity and Isomer Distribution for Benzoylation of Toluene with Benzoyl Chloride at 110°C

| Catalyst | Calcination temperature (°C) | Initial rate (×10³)[a] (mol/ l·min·g) | Methylbenzophenone (%) | | |
|---|---|---|---|---|---|
| | | | *ortho-* | *meta-* | *para-* |
| $FeSO_4$ | 500 | 2.4 | 20.1 | 3.8 | 76.1 |
| | 700 | 7.7 | 21.6 | 4.2 | 74.2 |
| | 900 | 1.0 | 22.3 | trace | 77.7 |
| $Fe_2(SO_4)_3$ | 500 | 1.4 | | | |
| | 700 | 10.1 | 14.0 | 2.1 | 83.9 |
| | 900 | 1.1 | 18.7 | 3.3 | 78.0 |

[a] Induction periods in all runs were below 6 min.

Table 2. The reaction rate in the benzoylation is expected to be lower in comparison with that in the benzylation because of the weak electrophilicity of the benzoyl cation, $C_6H_5CO^+$. In fact, it took more than 50 min to complete the 30% conversion at 110°C over the most active catalyst. The reaction curve is quite different from that in the benzylation, HCl evolution being nearly linear with time with very short periods of induction in all runs. These differences might be due to the different reaction mechanisms and/or the different catalytic actions. Both iron sulfates showed the highest activity when calcined at 700°C. Little difference can be seen in the isomer distribution over the catalysts with the different heat treatments. $AlCl_3$ was observed to produce 9.3% *o*-, 1.5% *m*-, and 89.3% *p*-form (*4*), while the present catalvsts gave about 20–22% of *o*-isomer.

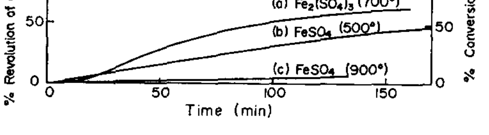


FIG. 2. Consumption of NaOH vs time recorded by a pH stat for benzoylation. Reaction temperature: 110°C. Catalyst: (a) 0.407, (b) 0.509, (c) 0.392 g. Figures in parentheses show the calcination temperatures.

In the previous work (*1a*), the reaction mechanism for the benzylation was explained on the basis of the concept in the homogeneous system, though our observations were carried out in the heterogeneous system. We again attempted to apply this concept to the benzoylation. Table 3 shows the $k_T/k_B$ (the ratio of rate in toluene and benzene) value and partial rate factors, $o_f$, $m_f$, $p_f$, which indicate the positional relative rate of reaction of benzene and toluene, calculated from $k_T/k_B$ and isomer ratio.[3] It is of considerable interest that the present catalysts gave surprisingly small values of $k_T/k_B$ and partial rate factors, compared with those of $AlCl_3$. From the observations by $AlCl_3$, the benzoylation reaction yields a relatively high $k_T/k_B$ with relatively low *meta* substitution, together with high *para* substitution, and in terms of the above interpretation, the benzoylation would be considered as a reaction of low "activity" and high "selectivity." This reflects the weak electrophilic nature of the benzoyl cation. Therefore, the cation is

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[3] Examples of calculation are shown as follows:

$$o_f = \%\,o\text{-} \times k_T/k_B \times 3/100;$$

$$p_f = \%\,p\text{-} \times k_T/k_B \times 6/100.$$

TABLE 3

Partial Rate Factors of Toluene with Benzoyl Chloride

| Catalyst | Solvent | $k_T/k_B$ | Isomer ratio (%) | | | Partial rate factors | | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | *ortho-* | *meta-* | *para-* | $o_f$ | $m_f$ | $p_f$ | |
| $FeSO_4$ (700°) | Toluene | 7.4 | 21.6 | 4.2 | 74.2 | 4.8 | 0.9 | 32.9 | Author |
| $Fe_2(SO_4)_3$ (700°) | Toluene | 6.3 | 14.0 | 2.1 | 83.9 | 2.6 | 0.4 | 31.7 | Author |
| $AlCl_3$ | $PhNO_2$ | 151 | 7.2 | 1.1 | 91.7 | 32.6 | 5.0 | 831 | *5* |
| $AlCl_3$ | PhCOCl | 110 | 9.3 | 1.49 | 89.2 | 30.7 | 4.8 | 589 | *6* |
| $AlCl_3$ | $CH_3NO_2$ | 153 | 8.1 | 1.2 | 90.7 | 37.3 | 5.5 | 835 | *7* |

considered to act as the relatively strong electrophilicity over the present catalysts, judging from the low values of $k_T/k_B$ and of partial rate factors, which show the low substrate and positional selectivities. This leads to the explanation of the relatively large formation of *ortho*-isomer despite the large steric requirements for the substituting species, $C_6H_5CO^+$.

Iron sulfate is decomposed to form iron oxide above 500°C (*8*). In an earlier paper (*1a*), it was tentatively interpreted that the benzylation was not catalyzed by the oxide surface, whereas the slight amount of sulfur remaining on the oxide upon the decomposition of sulfate salts was catalytically significant. It was also explained that the catalytic activities were not related to the surface area of the catalyst. Therefore, the specific surface areas and the sulfur content of the present catalysts were measured as shown in Tables 4 and 5, respectively. No correlation between the activities and surface areas can be seen. It can be known by calculation, using Fe and S contents in Table 5 and also referring to Mössbauer spectrum, that both ferrous and ferric sulfates are mostly kept in sulfate forms at 500°C of calcination, and decompose to form iron oxides at 700°C. Even though the small amount of sulfur remaining on the catalyst surface is considered to have an essential effect upon the catalytic action, it is not clear at this stage whether or not 0.15% of the sulfur content of iron sulfates heat-treated at 700°C, the most active catalyst, is reasonable. The iron sulfate calcined at 900°C, in which no sulfur is contained, caused both the benzylation and benzoylation reactions, though the rates were low.

In order to know the active sites of the catalyst in detail, Mössbauer experiments on ferrous sulfate, heat-treated at several temperatures, were performed. Obtained spectra are shown in Fig. 3 and their parameters are listed in Table 6. The spectrum of ferrous sulfate calcined in air at 300°C (a) shows two symmetric doublets identified as $Fe^{2+}$ and $Fe^{3+}$ which are assigned to $FeSO_4 \cdot H_2O$ and $FeSO_4 \cdot OH$, respectively (*9*). From absorption peak areas, the portions of them were 73% for $Fe^{2+}$ and 27% for $Fe^{3+}$. The spectrum (b) at 500°C of calcination temperature indicates

TABLE 4

Specific Surface Areas of Calcined Iron Sulfates and Ferric Oxide

| Catalyst | Calcination temperature (°C) | Area ($m^2/g$) |
|---|---|---|
| $FeSO_4$ | 500 | 66 |
| | 700 | 63 |
| | 900 | 49 |
| $Fe_2(SO_4)_3$ | 700 | 71 |
| $Fe_2O_3$[a] | 700 | 24 |

[a] The benzylation reaction over this catalyst was 40 times as slow as that of $Fe_2(SO_4)_3$ calcined at the same temperature (*1a*).

TABLE 5

Fe and S Contents of Calcined $FeSO_4$ and $Fe_2(SO_4)_3$ (Weight %)[a]

| Catalyst | Calcination temperature (°C) | Fe | S |
|---|---|---|---|
| $FeSO_4$ | 500 | 35.64 | 19.83 |
| | 700 | 69.68 | 0.15 |
| | 900 | 70.64 | 0 |
| $Fe_2(SO_4)_3$ | 500 | 28.61 | 23.91 |
| | 700 | 70.28 | 0.15 |
| | 900 | 71.89 | 0 |

[a] Theoretical value of S content: 21.1% for $FeSO_4$, 24.0% for $Fe_2(SO_4)_3$.

the presence of two types of $Fe^{3+}$. The sharp single peak corresponds to $Fe_2(SO_4)_3$ and the other six lines are attributed to $\alpha$-$Fe_2O_3$. These two components in the catalyst were also confirmed by means of X-ray diffraction method. On the other hand, the fractions of $\alpha$-$Fe_2O_3$ and $Fe_2(SO_4)_3$ are calculated as 17 and 83 wt%, respectively, by using the Fe and S contents shown in Table 5. From these results, the ratio of iron in $\alpha$-$Fe_2O_3$ to that in $Fe_2(SO_4)_3$ is about 1 to 2. This ratio is close to that determined from the Mössbauer spectrum. The spectra (c) and (d) show that the sample changed to form completely $\alpha$-$Fe_2O_3$ above 700°C.

TABLE 6

The Mössbauer Parameters of Ferrous Sulfates Heat-Treated at Several Temperatures

| Calcination temperature (°C) | Isomer shift[a] (mm/sec) | $1/2e^2qQ$ (mm/sec) | Interval magnetic field (kOe) |
|---|---|---|---|
| 300 | 1.04 ± 0.05 | 3.00 ± 0.05 | 0 |
| | 0.24 | 1.39 | 0 |
| 500 | 0.19 ± 0.1 | 0.00 | 0 |
| | 0.23 ± 0.05 | 0.30 | 488 |
| 700 | 0.19 ± 0.1 | 0.20 | 514 |
| 900 | 0.22 | 0.26 | 523 |

[a] Referred to metallic iron.

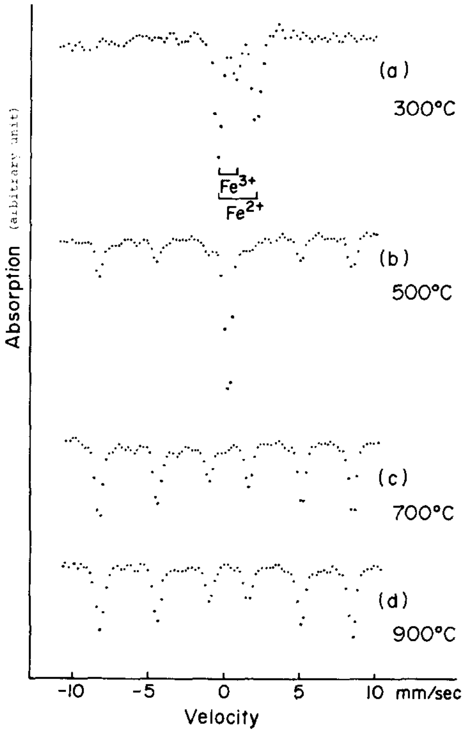

FIG. 3. Mössbauer spectra of ferrous sulfate calcined in air at 300 (a), 500 (b), 700 (c), and 900°C (d).

Since the ferric sulfate catalysts were not active at all until 400°C of calcination temperature and the activity rapidly increased with increasing of calcination temperature from 500 to 700°C (*1a*), $Fe^{3+}$ in the oxide structure must be catalytically essential. In fact, ferric sulfate is white until 400°C, indicating its sulfate color, whereas the sample begins to turn to reddish-brown indicating the oxide color, and finally changes to the color of iron oxide itself at 700°C of calcination.

It is quite interesting that the benzylation reaction did not occur at all over the ferrous sulfate catalyst calcined at 700°C at the reaction temperature of 200 or even 300°C in the gas phase.[4] It is inferred that

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[4] The reaction was carried out by a conventional flow method using nitrogen as carrier gas. A mixture of vaporized toluene and benzyl chloride in the equimolar and nitrogen were passed through the catalyst bed (1 g) at the flow rates of 5.4 ml/hr (as liquid) and 15 ml/min, respectively.

the present catalysts are active for the Friedel–Crafts reaction in the liquid phase. On the catalyst surface, a certain complex consisting of $Fe^{3+}$, $O^{2-}$, HCl, and others might be formed under the liquid reaction conditions and then act as a catalyst. Consequently, the induction period observed in the benzylation can be explained well as the period of formation of such a complex. However, this interpretation does not seem to apply to that of the short periods of induction with the slow reaction rate in the benzoylation. Since the $k_T/k_B$ value and partial rate factors in the benzoylation over the present catalyst differed exceedingly from those in the benzylation (*1a*) in comparison with those of Lewis catalysts such as $AlCl_3$ or $BF_3$, the catalytic actions on both reactions might be quite different.

If the above-mentioned complex is formed during the induction in the benzylation, the Mössbauer spectra of the catalyst during the period is considered to give different ones from those shown in Fig. 3. However, the spectrum of the ferrous sulfate catalyst calcined at 700°C under the same conditions as reaction was just similar to that in Fig. 3. The change of the catalyst surface caused during the period of induction might not have been enough in concentration to distinguish on the spectra.

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