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HIGH 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 showed surprisingly high catalytic activity and selectivity for the title reaction, and also catalyzed the benzoylation of toluene.

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) and this type of catalysts has been mostly used for the Friedel-Crafts reaction, which is one of the most studied of organic reactions.(3) Since this benzylation has been found to be catalyzed by solid acid catalysts such as nickel sulfate and alumina,(4) we have continued further investigations and found the unexpected effectiveness of ferrous and ferric sulfates.

The benzylation reaction was carried out with 50 ml of 0.5 M benzyl chloride in toluene and 0.3 g of accurately weighed iron sulfate, and its reaction rate was determined by amount of evolved HCl which was delivered by N_2 gas into water and titrated automatically. The iron sulfate catalyst was prepared by calcining a guaranteed reagent grade hydrate in air, and stored in a sealed ampoule until use. The products were analyzed and identified by G.C. comparison with the authentic samples, using a 45 m capillary column of Ucon LB-500-X.

In every case HCl evolution was linear with time, after a period of induction, up to over 50% completion, and the reaction afterwards followed a first order kinetics with respect to the benzyl chloride concentration. The results are shown in Figure. The products were 42% ortho-, 6% meta-, and 51% para-benzyltoluene with the almost negligible amount of polymer in all the analyzed runs shown in Figure. It can be seen that the higher calcination temperature, the higher catalytic activity and the less induction period. The activities are not entirely related to the acidities in the range of $pKa=-3.0\sim4.8$ measured by the n-butylamine titration method, whose maxima appeared around 200°C.(5) It should be noted that the observed rates obtained by alumina and sulfates of Co, Mn, Ni, and Cu, all calcined at 350°C, were below 0.019 mol l^{-1} min^{-1} g^{-1} at 100°C,(4) which were extremely small compared to the rates catalyzed by iron sulfates at 53.5°C or even at 30.5°C. 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 activity of Fe_2O_3 calcined at 700°C was examined since it was experimentally shown from weight loss that iron sulfates changed to their oxides by calcining at 700°C, and it was 0.031 mol l^{-1} min^{-1} g^{-1}, 40 times as small as that of $Fe_2(SO_4)_3$ calcined at the same temperature. It was worth noting that $FeSO_4$ and $Fe_2(SO_4)_3$ calcined at 700°C also caused the benzoylation of toluene with benzoyl chloride at the rates of 0.014 and 0.024 mol l^{-1} min^{-1} g^{-1}, respectively, at 100°C.

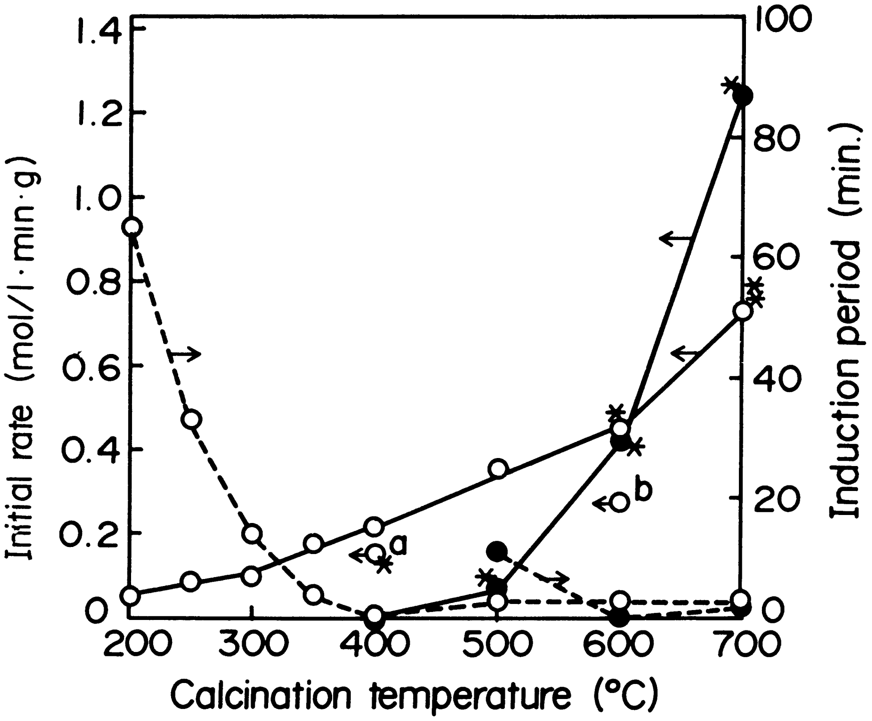

Figure. Catalytic activities and induction periods of ferrous and ferric sulfates versus calcination temperature, at 53.5°C, ○ ; $FeSO_4$, ● ; $Fe_2(SO_4)_3$. a, b; at 30.5° and 34.5°C, with 59 and 13 min. of induction periods, respectively.

* The products were analyzed.

** The reaction completed 80% in 2 min.

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