High Catalytic Activity of Calcined Iron Sulphates for the Polycondensation of Benzyl Chloride

By KAZUSHI ARATA,[†] AKIO FUKUI,[‡] and ISAMU TOYOSHIMA*[§]

([†]*Hokkaido University of Education, Hakodate, Japan* 040, [‡]*Sumitomo Chemical Co. Ltd., Central Research Laboratory Takatsuki, Japan* 569, [§]*Research Institute for Catalysis, Hokkaido University, Sapporo, Japan* 060)

Summary Ferrous and ferric sulphate hydrates, when calcined in air at 700 °C, produce catalysts which effect the polymerisation of benzyl chloride at room temperature in a few seconds; the polymer is stable up to 400 °C and has predominantly *para*-polybenzyl structure.

POLYCONDENSATION of benzyl chloride with simultaneous evolution of hydrogen chloride is known to be catalysed by Lewis acids such as stannic chloride.[1,2] We have found that calcined iron sulphate is exceedingly active for this polymerization.

The iron sulphate catalyst was prepared by calcining a guaranteed reagent grade hydrate in a Pyrex glass or quartz tube for 3 h in air and stored in ampoules. When the catalyst (*ca.* 0·2 g), heat-treated at 700 °C, was added to 2 ml of benzyl chloride at room temperature, polymerization occurred immediately with evolution of HCl. The reaction was complete in < 1 min to give a brownish, dry and foamy solid which is soluble in benzene but insoluble in acetone. The time required for the formation of the polymer depends on the calcination temperature of iron sulphate as shown in the Table; the catalyst calcined at 700 °C appears to be the most active. A different batch of the catalyst purchased from the

TABLE

Catalytic activity of calcined sulphates of iron, nickel, and cobalt and of ferric oxide for the polymerization of benzyl chloride at room temperature.[a]

Catalyst	Calcination temperature (°C)	Amount of catalyst used (g)	Reaction time (s)
$FeSO_4$	200	0·15	None[b]
,,	300	0·12	4740
,,	500	0·11	72
,,	700	0·19	20
,,	800	0·20	None[b]
,,	900	0·23	None[b]
$Fe_2(SO_4)_3$	500	0·30	None[b]
,,	600	0·28	500
,,	700	0·07	35
,,	800	0·24	None[b]
Fe_2O_3	700	0·11	None[b]
$NiSO_4$	700	0·21	None[b]
,,	900	0·11	None[b]
$CoSO_4$	700	0·25	None[b]
,,	900	0·13	None[b]

[a] 2 ml of benzyl chloride was used of each reaction. [b] Reaction did not take place over a period of 1 week.

same supplier showed similar activity. It has been shown that ferrous sulphate calcined in air at 700 °C consists of 100% Fe^{3+} in the oxide form.[3] However, ferric oxide prepared by calcining its hydroxide at 700 °C showed no catalytic activity even over a period of one week. ESCA studies of the present catalysts show that iron sulphate completely decomposes to form α-Fe_2O_3 at 675—700 °C, and then recrystallization proceeds rapidly.[4] A small amount of sulphur (0·15 wt %) which remains in the catalyst after decomposition, exists as SO_4^{2-} on the surface.[4] Nickel and cobalt oxides show no catalytic activity, although the elements belong to the same group in the Periodic Table as iron.

Elemental analysis and i.r. and n.m.r. spectroscopy indicate that the purified product of the reaction is predominantly linear *para*-substituted polymer [δ 7·15 (br s, 4H, phenylene H) and 4·85 (s, 2H, CH_2); ν (neat) 3000, 2900, 1600, 1490, 1450, 730, and 700 cm^{-1}]. The limiting viscosity number, determined in toluene solution, is $[\eta] = 0{\cdot}048$ and the molecular weight is 3550. Thus the degree of polymerization is *ca.* 40. The D.T.A. and T.G.A. analyses in air show that the polymer is thermally stable up to 400 °C above which decomposition occurs. The polymer decomposes almost completely at 660 °C.

Specific surface areas of the catalysts were determined by the BET method using nitrogen at −196 °C.[5] The surface area of the catalyst bears no relationship with its catalytic activity [surface areas: 66, 63, 49, and 71 $m^2\,g^{-1}$ for $FeSO_4$ (calcined at 500 °C), $FeSO_4$ (700 °C), $FeSO_4$ (900 °C), and $Fe_2(SO_4)_3$ (700 °C), respectively]. Use of anhydrous aluminium chloride, a typical Lewis acid catalyst, results in a whitish, oily material after several hours, whose appearance is different from that of the polymer obtained by using the iron sulphate catalyst. The molecular weight of this material could not be determined. It has been reported that a branched polymer is obtained by using stannic chloride as a catalyst, but this polymer has molecular weight in the range 1000—1200 and the reaction required several hours for completion.[1,2]

(*Received*, 24*th October* 1977; *Com.* 1106.)

[1] L. Valentine and R. W. Winter, *J. Chem. Soc.*, 1956, 4768.

[2] N. Grassie and I. G. Meldrum, *European Polymer J.*, 1971, **7**, 629.

[3] K. Arata, K. Yabe, and I. Toyoshima, *J. Catalysis*, 1976, **44**, 385.

[4] K. Yabe, K. Arata, and I. Toyoshima, unpublished results.

[5] S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.