CHEMISTRY LETTERS, pp. 1479-1480, 1980.

HIGH CATALYTIC ACTIVITY OF IRON OXIDE FOR BENZYLATION, t-BUTYLATION, AND ACETYLATION OF TOLUENE WITH BENZYL, t-BUTYL, AND ACETYL CHLORIDES

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Iron oxides obtained by calcining at 300-500°C $Fe(NO_3)_3$ or iron hydroxides, precipitated by hydrolyzing $FeCl_3$ and $Fe(NO_3)_3$ with ammonia, showed exceedingly high catalytic activities for the title reactions at room temperature.

Alkylations such as benzylation and t-butylation of toluene with their corresponding chlorides are known to be catalyzed by Lewis-type catalysts such as anhydrous $AlCl_3$ and $FeCl_3$,$^{1)}$ which have been mostly used for the Friedel-Crafts reaction.$^{2)}$ Previously we reported that iron sulfates heated at high temperature are active for the benzylation.$^{3)}$ We have continued further investigations of solid catalysts, especially metal oxides, active for the Friedel-Crafts reaction and now wish to report that iron oxides prepared are exceedingly active for the alkylations and even for the acetylation of toluene with acetyl halides.

$Fe(OH)_3$-I and -II were precipitated by hydrolyzing $FeCl_3$ and $Fe(NO_3)_3 \cdot 9H_2O$, respectively, with aqueous ammonia. They were washed and then dried at 100°C for 24 h. $Fe(NO_3)_3$ was prepared by heating $Fe(NO_3)_3 \cdot 9H_2O$ (Wako Pure Chemical Co.) at 150°C for 2-3 h. The dried catalysts were powdered below 100 mesh and then calcined in Pyrex glass tubes in air for 3 h. The catalyst thus prepared was sealed in an ampoule and stored until use. The benzylation, t-butylation, and acetylation reactions were carried out with 50 ml of 0.5 M toluene solution of benzyl chloride, t-butyl chloride, and acetyl chloride, respectively, and 0.1 g (for benzylation and t-butylation) or 0.5 g (for acetylation) of catalyst with stirring at room temperature. At appropriate time intervals, a small amount of the sample was taken out by a 1 ml syringe, and separated from the catalyst. The products were analyzed by gas chromatography using 2 m columns of silicone SE 30 (for benzyltoluenes) and PEG 1000 (for t-butyltoluenes). In the case of acetylation, the reaction mixture (50 ml) was washed with water several times after removing the catalyst and dried; the products were analyzed using a 2 m column of TCP with ethylbenzene as an internal standard.

Table 1 shows % conversions of both the alkylations and the acetylation. The iron oxides prepared by calcining $Fe(OH)_3$-I, -II , and $Fe(NO_3)_3$ at 300-500°C showed surprisingly high activities for the benzylation. The catalysts treated at 300 or 400°C were also examined in the t-butylation of toluene with t-butyl chloride, and all the reactions were completed in 10-30 min. The isomer distributions of alkyltoluenes obtained were 42% o-, 6% m-, and 52% p-benzyltolene for the benzylation, and 3% m- and 97% p-t-butyltoluene for the t-butylation.$^{4)}$ Commercially available anhydrous $FeCl_3$ showed 97% conversion in 10 min for the benzylation under the same conditions.

The catalysts treated at 300°C were next examined in the acetylation of toluene with acetyl halides. The remarkable yields of metylacetophenones were obtained at room temperature, though the reaction rate is expected to be quite slow. The acetylation with acetyl bromide was faster than that

Table 1. Conversion(%) in the benzylation, t-butylation, and acetylation of toluene at room temperature

Catalyst	Temp of calcn. (°C)	Benzylation				t-Butylation				Acetylation		
		Reaction time (min)				Reaction time (min)				Time (h)		
		4	6	10	30	6	10	20	30	2	4	6
$Fe(OH)_3$-I	300	100$^{a)}$				25	95	100				11
	400	100$^{b)}$				85	100					
	500	33	95	100								
	600				0$^{c)}$							
$Fe(OH)_3$-II	200				0							
	300	77	100			30	100			12	30$^{d)}$	28
	400	100										
$Fe(NO_3)_3$	300	95	100			10	15	90	100			15
	400	8	30	100								
	500		20	75	100							

a) The reaction was completed in 2 min. b) 90% in 2 min. c) 0% in 2 h. d) Reaction with acetyl bromide as acetylating reagent.

with acetyl chloride. The product distribution was 3% o- and 97% p-methylacetophenone together with trace amount of the meta-isomer.

The catalysts prepared by calcining commercial $Fe(OH)_3$ (Kokusan Chemical Works) and Fe_2O_3 (Wako Pure Chemical Co.) at 350°C were inactive for the benzylation (0% conversion in 2 h). By differential thermal and X-ray diffraction analyses, these commercial materials were found to be crystallized iron(III) oxides in contrast with the present highly active catalysts, and thus it appears likely that the amorphous iron oxide is catalytically active for the reactions.

It seems that iron chloride was newly formed on the catalyst surface because of the probable reaction between iron oxide and the chlorides or HCl evolved by the reactions. Thus, the iron chloride is supposed to act as catalyst. Other metal oxides such as Al_2O_3, TiO_2, NiO, and SnO_2 were prepared and examined in the acetylation,$^{5)}$ since $AlCl_3$, $TiCl_4$, $NiCl_2$, and $SnCl_4$ are well used as the catalysts for the Friedel-Crafts alkylations and acylations.$^{1)}$ However, those oxides were found to be inactive (0% conversion in 24 h).

References and Notes

1) G. A. Olah,"Friedel-Crafts Chemistry," Wiley-Interscience, New York and London (1973).

2) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I-IV, Wiley-Interscience, New York and London, 1963-1964.

3) K. Arata and I. Toyoshima, Chem. Lett., 1974, 929.

4) The products were analyzed by gas chromatography using 5 m (for benzyltoluenes) and 3 m (for t-butyltoluenes) columns of Bentone 34 + DDP.

5) The oxides were prepared by calcining their hydroxides at 400°C under air. The hydroxides were precipitated by hydrolyzing $Al(NO_3)_3$, TiCl, $Ni(NO_3)_2$, and $SnCl_4$ with aqueous ammonia, washed, and dried. The acetylation reaction was carried out with 1 g of the catalyst.

(Received September 1, 1980)