

ACETYLATION OF TOLUENE WITH ACETYL CHLORIDE AND BROMIDE
CATALYZED BY CALCINED IRON SULFATE ACTIVATED BY EXPOSING
TO A MIXTURE OF BENZYL CHLORIDE AND TOLUENE

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The catalyst prepared by heating FeSO_4 in air at 700 or 800°C, followed by exposing to benzyl chloride in toluene at 60°C showed high activity for the title reaction.

Acetylation of toluene and benzene with acetyl halides, in which some of their products serve as valuable materials for perfume and cosmetic, has been performed with Lewis-type catalysts such as anhydrous aluminum chloride and ferric chloride.^{1,2)} This reaction is generally carried out under the homogeneous system by use of, at least, an equimolar amount of the catalyst for acetylating agent. We have found that the acetylation of toluene with acetyl halide with a new catalyst at room temperature under the heterogeneous system gave methylacetophenones in good yields.

The catalyst was prepared as follows : $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (guaranteed grade) was heated at 150°C for 1 h, powdered below 100 mesh, and then calcined at various temperature for 3 h in air. The activation of the catalyst was performed by heating a mixture of toluene (50 ml), the catalyst (1 g) and benzyl chloride (1 ml) at 60°C for 1 h. After cooling, acetyl chloride or bromide (0.025 mole) was added to the mixture, and the whole mixture was stirred at room temperature for 15-180 min. The catalyst was removed by filtration and the filtrate was washed with water and dried. Products were analyzed by gas chromatography using a 1 m column of tricresyl phosphate on Celite 545 with benzene as an internal standard.

Iron sulfate calcined at any temperature was inactive at all for the acetylation at room temperature unless otherwise activated. Table 1 shows the yield of the products. The catalytic activity of activated FeSO_4 changed remarkably by the calcination temperature. The sulfates calcined at 500, 600 and 900°C showed low activity. However, the considerable yield, 68 %, of methylacetophenones was obtained over the catalyst prepared by calcining at 700°C with both acetyl chloride and bromide, and the sulfate calcined at 800°C gave methylacetophenones in more than 90 % yield, though its reaction rate was slower than that using the catalyst calcined at 700°C. The catalysts treated at 500 and 600°C were found to be soluble in the reaction mixture, and that at 700°C was slightly soluble, while the catalysts calcined at 800 and 900°C were insoluble. The isomer distribution of

Table 1. Yield (%) of o-, m- and p-Methylacetophenone in the Acetylation of Toluene at Room Temperature

Catalyst	Temp. of calcn. (°C)	Acetylating reagent	Yield (%)						
			Reaction time (min)						
			15	30	60	90	120	180	300
FeSO ₄	500	CH ₃ COCl	12	13					
	600	CH ₃ COCl	17		16				
	700	CH ₃ COCl	52		68		68		
	700	CH ₃ COBr	61	65	67				
	700 ^{a)}	CH ₃ COBr							0
	800	CH ₃ COCl			31	54	88	<u>90</u>	
	800	CH ₃ COBr	13	34	87		<u>92</u>		
	900	CH ₃ COCl			1		8		

a) Without treatment with benzyl chloride.

methylacetophenone was 2 % ortho-, 1 % meta-, and 97 % para-form in all the performed runs.

FeCl₃ and AlCl₃ were used instead of the present catalysts under similar conditions, giving acetophenones in 24 and 29 % yields, respectively, which are quite close to the expected maximum yields estimated from the molar amounts of these catalysts and the acetylating reagent.

It is considered that the catalyst surface was activated by complicated interactions with benzyl chloride and HCl evolved by the benzylation of toluene with benzyl chloride.³⁾ A different catalyst, which was prepared by separating FeSO₄ (700°) from the mixture of benzyl chloride and toluene after the activation, followed by washing with toluene and drying, produced only 10 % of methylacetophenones in 2 h. As for other alkyl halides than benzyl chloride, t-butyl and isopropyl chlorides were examined, but these halides did not activate the catalysts.

References

- 1) E. H. Man and C. R. Hauser, J. Org. Chem., 17, 397 (1952).
- 2) G. A. Olah and S. Kobayashi, J. Am. Chem. Soc., 93, 6964 (1971).
- 3) K. Arata, K. Yabe, and I. Toyoshima, J. Catal., 44, 385 (1976).

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