

# Acylation of Toluene with Acetic and Benzoic Acids catalysed by a Solid Superacid in a Heterogeneous System<sup>1</sup>

Makoto Hino<sup>a</sup> and Kazushi Arata<sup>b\*</sup>

<sup>a</sup> Hakodate Technical College, Tokura-cho, Hakodate 042, Japan

<sup>b</sup> Hokkaido University of Education, Hachiman-cho, Hakodate 040, Japan

A solid superacid, which was prepared by exposing  $Zr(OH)_4$  to  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  followed by calcining in air at  $650^\circ\text{C}$ , was catalytically active in the acylation of toluene with acetic and benzoic acids in a heterogeneous system; this catalyst was also active for the reaction using ethyl and methyl esters as the acylating reagent.

In Friedel–Crafts acylation the reaction is generally performed with an acid chloride as the acylating reagent and with  $AlCl_3$  as the catalyst; the catalyst melts and becomes inactive owing to its co-ordination to the carbonyl group of the product as the reaction proceeds. The acid chloride is synthesized from the corresponding acid; thus using the carboxylic acid directly as the acylating agent could be advantageous.

We have previously reported that solid superacid catalysts with an acid strength of up to  $H_0 \leq -16.04$  were obtained by adsorbing the sulphate ion onto  $Zr(OH)_4$ ,  $Hf(OH)_4$ , and  $H_4TiO_4$  followed by calcination above  $500^\circ\text{C}$ .<sup>2–6</sup> In this communication, we report the acetylation and benzylation of toluene with acetic and benzoic acids and with benzoic anhydride over the superacid. We found that the acid catalyst of  $ZrO_2$  with an acid strength of  $H_0 \leq -16.04$  is most effective in the reactions, even for the reactions using ethyl and methyl esters as acylating reagents.

The catalysts were prepared as follows:<sup>2–6</sup>  $Zr(OH)_4$  was obtained by hydrolysing  $ZrOCl_2 \cdot 8H_2O$  with aqueous ammonium hydroxide, washing the precipitate, and drying at  $100^\circ\text{C}$ ;  $H_4TiO_4$  was obtained by dissolving titanium(IV) isopropoxide in aqueous nitric acid, hydrolysing with aqueous ammonia, washing, and drying at  $100^\circ\text{C}$ . The hydroxides (2 g), powdered below 100 mesh, were exposed to  $0.5 \text{ M H}_2\text{SO}_4$  ( $30 \text{ cm}^3$ ) on a filter paper followed by drying, calcining in a Pyrex tube in air for 3 h, and finally sealing in an ampoule until use.

Benzylation of toluene with benzoic acid was performed at reflux temperature over  $SO_4^{2-}/ZrO_2$  calcined at  $500\text{--}800^\circ\text{C}$ . The reaction was carried out with a mixture of acid ( $8.2 \times 10^{-4} \text{ mol}$ , 0.1 g),<sup>†</sup> toluene ( $12.5 \text{ cm}^3$ ), and catalyst (0.25–0.27 g) with stirring. The catalyst heat-treated at  $650^\circ\text{C}$  [ $SO_4^{2-}/ZrO_2$  ( $650^\circ\text{C}$ )] showed the maximum activity, the yield of methylbenzophenone being 6.5% for 3 h and 12% for 6 h. This catalyst has the highest acid strength ( $H_0 \leq -16.04$ ) among the solid superacids, and  $SiO_2\text{--}Al_2O_3$ , whose acid strength is  $-12.70 < H_0 \leq -11.35$ ,<sup>2,3</sup> was inactive under the same conditions. The  $SO_4^{2-}/TiO_2$  catalyst heat-treated at  $525^\circ\text{C}$ , whose acidity is  $-16.04 < H_0 \leq -14.52$ ,<sup>6</sup> showed low activity (3% yield for 6 h). It is considered that acid sites stronger than *ca.*  $H_0 = -15$  are needed for the formation of the acyl cation ( $RCO^+$ ) from a carboxylic acid.

The reaction was carried out with the  $SO_4^{2-}/ZrO_2$  ( $650^\circ\text{C}$ ) catalyst at  $180^\circ\text{C}$  using an autoclave. The yield of methylbenzophenone was 34% for 1 h and 60% for 3 h; the yield increased to over 60% with time under the present conditions. The product distribution was 30–35% *o*-, 5% *m*-, and 60–65% *p*-methylbenzophenone in every run, and no by-products were detected.

The benzylation was carried out with benzoic anhydride ( $8.2 \times 10^{-4} \text{ mol}$ , 0.18 g). As is shown in Figure 1, the reaction

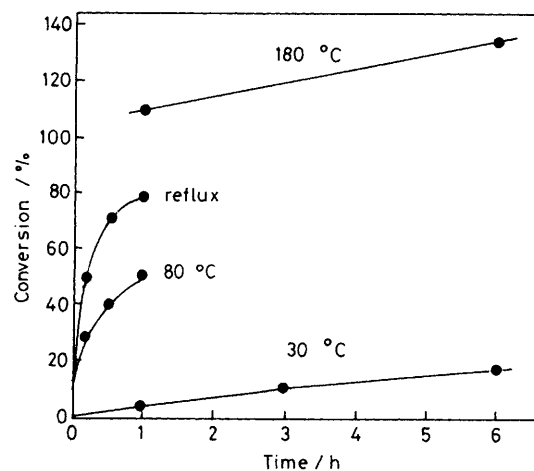


Figure 1. Benzylation of toluene with benzoic anhydride.  $SO_4^{2-}/ZrO_2$  ( $650^\circ\text{C}$ ): 0.24–0.27 g; benzoic anhydride: 0.18 g; toluene:  $12.5 \text{ cm}^3$ .

Table 1. Acetylation of toluene with acetic acid at  $280^\circ\text{C}$ .<sup>a</sup>

Molar ratio (acid: toluene)	Conversion/ %	Selectivity to ketone/ %	Isomers/ %		
			<i>o</i> -	<i>m</i> -	<i>p</i> -
1:4	20	87	19	10	71
1:8	29	88	19	10	71
1:16	51	89	16	13	71
1:32	67	82	10	21	69
1:16 <sup>b</sup>	25	100			

<sup>a</sup>  $SO_4^{2-}/ZrO_2$  ( $650^\circ\text{C}$ ): 1 g; flow rate:  $1.16 \text{ cm}^3 \text{ h}^{-1}$ ;  $N_2$  carrier:  $10 \text{ cm}^3 \text{ min}^{-1}$ . <sup>b</sup> Acetylation of benzene with acetic acid at  $250^\circ\text{C}$ .

took place readily; marked conversion was observed even at  $30^\circ\text{C}$ . Benzylation also seems to be caused by the benzoic acid produced. Therefore conversion  $>100\%$  is observed when the reaction occurs at  $180^\circ\text{C}$  as illustrated in Figure 1. The catalyst was removed during the reaction, and the mixture was again heated, but it failed to react further. Therefore, the present catalytic reaction is heterogeneous. Increasing the amount of the acyl reagent while keeping the catalyst quantity constant, showed the present reaction to be indeed catalytic. The isomer distribution of the product was 25–30% *o*-, 2–4% *m*-, and 66–73% *p*-methylbenzophenone.

The present catalyst was active in benzylation using esters as the acylating reagent; the  $SO_4^{2-}/ZrO_2$  ( $650^\circ\text{C}$ ) catalyst gave 2.5% yield with ethyl benzoate and 1.0% with methyl benzoate after 3 h at reflux temperature (ester  $8.2 \times 10^{-4} \text{ mol}$ , toluene  $12.5 \text{ cm}^3$ , catalyst 0.25 g). Thus, the reactivity with acylating reagents is  $(PhCO)_2O \gg PhCO_2H > PhCO_2Et > PhCO_2Me$ .

<sup>†</sup> The solubility of benzoic acid in toluene is low: 0.2–0.3 g in  $10 \text{ cm}^3$  at most.

The acetylation of toluene with acetic acid was also performed in a flow system. After the  $\text{SO}_4^{2-}/\text{ZrO}_2$  (650 °C) catalyst was heat-treated in a reactor at 350 °C for 1.5 h in a stream of nitrogen, a vapourized mixture of toluene and acid was passed through the catalyst bed. Table 1 shows the results between 150 and 180 min; the yield of product, methylacetophenone, was almost steady until 300 min. Small amounts of several by-products, alkylated derivatives of toluene, were produced.

It is concluded from the activity and selectivity to acetylation that the present catalyst can be used in acetylation with carboxylic acids in vapour phase. Acetylation with ethyl acetate formed 23% methylacetophenone under the conditions stated in Table 1 (acid : toluene 1 : 16).

Specific surface areas of  $\text{SO}_4^{2-}/\text{ZrO}_2$  (500, 650, and 800 °C) and  $\text{SO}_4^{2-}/\text{TiO}_2$  (525 °C) were 187, 124, 41, and 144  $\text{m}^2/\text{g}$ , respectively, the relative activity per unit area for the reaction of toluene and benzoic anhydride being 1.0 : 4.5 : 4.7 : 1.3. X-Ray photoelectron and i.r. spectra showed the  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalysts to possess a bidentate sulphate ion co-ordinated to the metal,<sup>5,6</sup> and the double bond nature of S=O in the

complex was shown to be much stronger than that of simple metal sulphates.<sup>7</sup> Thus, the adsorption site appears likely to be a strong Lewis acid of  $\text{Zr}^{4+}$  created by the inductive effect of S=O or a Brønsted acid formed by the adsorption of water on the  $\text{Zr}^{4+}$ .

Received, 6th September 1984; Com. 1267

## References

- 1 For previous articles in the series 'Solid Catalysts Treated with Anions,' see M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, 1984, 1037.
- 2 M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, 1979, 1148; 1980, 851.
- 3 M. Hino, S. Kobayashi, and K. Arata, *J. Am. Chem. Soc.*, 1979, **101**, 6439.
- 4 K. Arata and M. Hino, *React. Kinet. Catal. Lett.*, 1984, **25**, 143.
- 5 M. Hino, K. Arata, and K. Yabe, *Shokubai*, 1980, **22**, 232.
- 6 K. Arata and M. Hino, *Hyomen*, 1981, **19**, 75.
- 7 T. Yamaguchi, A. Mitoh, K. Akiyama, and K. Tanabe, *Shokubai*, 1983, **25**, 127.