NOTES

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Friedel-Crafts Benzylation of Toluene with Benzyl Chloride Catalyzed by Metal Oxides

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Synopsis. Metal oxides were found to catalyze significantly the Friedel-Crafts type benzylation of toluene with benzyl chloride with a selectivity similar to that occurring with metal sulfates.

The benzylation of toluene with benzyl chloride, which is a typical example of Friedel-Crafts alkylations and is known to proceed over Lewis-type catalysts such as anhydrous aluminum chloride and gallium bromide,[1] has been found to be catalyzed by metal sulfates: $NiSO_4$, $MnSO_4$, etc.[2] Iron sulfates especially showed an unexpected effectiveness for this reaction.[3,4] The selectivity, however, of these studied catalysts was almost the same, indicating the analogous reaction mechanism. In order to extend the scope of this reaction, we have examined the catalytic activity as well as the selectivity of these metal oxides: ZnO, TiO_2, ZrO_2, and TiO_2–ZrO_2.

Experimental

Experiments which do not overlap with those reported in the previous paper[4] are described here.

Preparation of Catalysts. ZnO was prepared by calcining its hydroxide in air at 400 °C for 3 hr. The hydroxide was precipitated by adding 2 M aqueous ammonia to an aqueous solution of zinc chloride (1 M), followed by washing thoroughly with water until no chloride ion was detected in the filtrate and drying at 120 ° for 24 hr. TiO_2, ZrO_2, and TiO_2–ZrO_2 (molar ratio=1 : 1) were prepared by calcining H_4TiO_4, $Zr(OH)_4$, and H_4TiO_4-$Zr(OH)_4$, respectively, in air at 500 °C for 3 hr. These materials were precipitated by heating a mixed aqueous solution (5 l of 0.2 M) of titanium tetrachloride, zirconium oxychloride, or both chlorides and an excess amount of urea (300 g) on a boiling water bath for 6—9 hr, followed by thorough washing and drying at 110 °C for 30 hr.

Results and Discussion

As observed in the case of metal sulfates, the initial part of the HCl evolution was linear with time after a slight period of induction, and the over-all reaction followed first order reaction kinetics with respect to the benzyl chloride concentration.

Table 1 summarizes the initial rates and the relative rates, together with the pertinent data taken from our previous study.[2] It is shown that the present metal oxides, solid acid catalysts,[5,6] are quite active for this Friedel-Crafts reaction, especially TiO_2–ZrO_2, which is more than 400 times as active as $NiSO_4$. The products were very similar in distribution with an almost negligible amount of polymer, as shown in Table 2. This product distribution is quite similar to that by sulfates of Ni, Mn, and other metals.[2–4] This similarity of selectivity implys that the catalytic actions upon this benzylation are the same on those studied catalysts: that is, the catalytic mechanism is independent of the species of catalyst and reaction rate. Since an induction period, which is presumably the period of HCl adsorption on the catalyst surface, was observed in every reaction, it is supposed that the adsorbed HCl acts as a true catalyst. This model is attractive in explaining the similarity of the catalytic action. However, $AlCl_3$, a typical Lewis catalyst, gave a quite different selectivity (10.2% *ortho*-, 69.0% *meta*-, and 20.8% *para*-isomer) under the heterogeneous reaction condition.[2] Therefore, it is concluded that solid acids such as metal sulfates and oxides give the same selectivity arising from the same catalytic actions for the Friedel-Crafts type benzylation.

TABLE 1. CATALYTIC ACTIVITIES OF METAL OXIDES FOR BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE AT 100 °C

Catalyst	Initial rate (mol/l·min·g)	Relative rate (ZnO=1)
ZnO	0.036	1.00
TiO_2	0.30	8.3
ZrO_2	0.11	3.1
TiO_2-ZrO_2	0.48[a]	13.3
$MnSO_4$[b]	0.0073	0.2
$NiSO_4$[b]	0.0012	0.03

a) The reaction was 80% completed in 5 min.
b) Ref. 2.

TABLE 2. ISOMER DISTRIBUTION OF BENZYLTOLUENE

Catalyst	Mol %		
	Ortho-	*Meta-*	*Para-*
ZnO	43.0	6.0	51.0
TiO_2	46.5	7.3	46.1
ZrO_2	44.5	7.8	47.8
TiO_2-ZrO_2	43.2	7.7	49.1

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References

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