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SYNTHESIS OF ESTERS FROM ACETIC ACID WITH METHANOL, ETHANOL, PROPANOL, BUTANOL, AND ISOBUTYL ALCOHOL CATALYZED BY SOLID SUPERACID[1]

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A solid superacid catalyst, which was obtained by exposing $Zr(OH)_4$ to 1N H_2SO_4 and then calcining in air at 500-750°C, was found to be highly active for the heterogeneous title reactions at 30-45°C. The reactions with the used catalyst gave identical results with those using freshly activated catalyst.

In the esterification of carboxylic acids with alcohols, the reaction is well known to be catalyzed by protonic acid, sulfuric acid being usually used. The homogeneous reaction using sulfuric acid industrially involves many problems to be solved: for instance, corrosion of reaction vessel, and difficulty in treatment of sulfuric acid after reaction because of the environmental problem. Thus, it is desired to use the heterogeneous process using solid acid catalyst in place of sulfuric acid. Recently, we reported that solid superacids were prepared by treating $Fe(OH)_3$, H_4TiO_4 or $Zr(OH)_4$ with sulfate ion followed by calcination above 500°C, the materials with superacidity up to $H_0 \leqq -16.04$ being obtained.[2] In continuation of our interest in the catalytic ability of the superacid, we wish to report the results of a convenient esterification catalyzed by the superacid.

The catalyst was prepared as follows. $Zr(OH)_4$ was obtained by hydrolyzing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia, washing, drying at 100°C, and powdering the precipitates to below 100 mesh grains. The hydroxides (2 g) were exposed to 1N H_2SO_4 (30 ml) 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. The esterification was carried out with 30 ml of 1.04 M acetic acid in alcohol and 0.25g of the catalyst with stirring. The yield of esters formed was estimated from the decrease of acetic acid by titration or from gas chromatographic analysis with benzene as an internal standard after removal of the catalyst by filtration.

The esterification of acetic acid with ethanol was carried out at 30-60°C over the catalysts heat-treated at various temperatures; the results are shown in Table 1. The catalysts treated at 500-750°C were active for the reaction at 30°C, the material calcined at 575°C being most active. The catalyst gave ethyl acetate in 93% yield at 60°C for 24 h. The yield of ester increased with time in every reaction. SiO_2-Al_2O_3 (Nikki Chemical Co., 15% Al_2O_3, heat-treated at 500°C), which is well used as one of the solid acid catalysts with the highest surface acidity, was inactive at 30°C (0% yield after 24 h).

Table 1. Esterification of Acetic Acid with Alcohols

Alcohol	Calcination temp of catalyst, °C	Reaction temp, °C	Yield of esters, %[a)] Reaction time, h 3	8	24
EtOH	500	30			34
	575	30			50
	650	30			39
	750	30			22
	575	45	32	45	78
	575	60	45	72	93
MeOH	575	30	45	68	
MeOH	575	45	62	85	
1-PrOH	575	45	26	40	
1-BuOH	575	45	26	42	
i-BuOH	575	45	13	28	

a) Yield based on acetic acid.

The catalyst treated at 575°C was examined in the esterification of the acid with methanol, 1-propanol, 1-butanol and 2-methyl-1-propanol. The remarkable yields of esters were obtained at 45°C as is shown in Table 1. Any products other than esters were not detected in every reaction.

Regeneration of the used catalyst (treated at 575°C) was examined; that is, after filtration, the catalyst was washed with methanol, calcined at 575°C for 3 h, and then used for the reaction of acetic acid with methanol at 60°C for 1 h. The yield of methyl acetate was 63% compared with 65% for the first reaction. Repeating the reaction with the used catalyst was also examined in the following way; after filtration, the catalyst was washed with ethanol, then was used for the reaction of acetic acid with ethanol at 45°C for 8 h. The yield of ethyl acetate was 40%: cf. 43% for the first run. Thus, no reactivation of the catalyst is needed since the catalytic activity remains unchanged for the repeated operation.

In the described esterification method, the present heterogeneous catalyst provides a very simple work up as Nafion-H, a solid perfluorinated resinsulfonic acid, which is also a very effective catalyst for the heterogeneous esterification.[3] Nafion-H was examined in the reactions of methanol and ethanol at 30°C under the same conditions. The yields of methyl and ethyl esters were 69% after 8 h and 47% after 24 h, respectively, which are quite close to the present results.

References

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