Letter

Liquid phase hydrogenation of carboxylic acid catalyzed by supported bimetallic Ru–Sn–alumina catalyst: effects of tin compounds in impregnation method

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Abstract

The Ru–Sn bimetallic system was one of the effective catalysts for selective hydrogenation of –C=O group in carboxylic acids. The type of tin compound used for the preparation of the bimetallic catalysts was important for the hydrogenation activity. The effective materials were K_2SnO_3 and Na_2SnO_3 for the hydrogenation of –C=O.

Catalytic hydrogenation of carboxylic acids or its esters on supported bimetallic catalyst has been discussed in many reports. For example, Basset et al. [1] have reported the hydrogenation of ethyl acetate by using Rh–Sn catalyst. The authors [2] have reported that C=O in methyl oleate dimer was hydrogenated to alcohol by using Rh–Sn catalyst. Mizukami et al. [3] have reported the hydrogenation of oleic acid to 9-octadecen-1-ol by using Ru–Sn catalyst prepared by the sol–gel method.

Here we examine the hydrogenation of rosin which is an essentially abietic acid to the corresponding useful rosin alcohol on the industrial

level. The reaction scheme is shown in Fig. 1. The sol–gel method by Mizukami [3] and the method using organometallic compounds by Basset [1] are not readily adaptable for practical applications to industrial processes. We report herein the hydrogenation of rosin to rosin alcohol by using Ru–Sn catalyst prepared by impregnation by the use of a nontoxic Sn compound in a heterogeneous system in the liquid phase, and the effects of the type of Sn compound used.

Alumina was soaked in an aqueous solution of K_2SnO_3. The mixture was aged for 12 h at room temperature, and dried. The powder obtained was soaked in a 2-propanol solution of $Ru(NO)(NO_3)_3$. The mixture was aged for 12 h at room temperature, and dried. The powder

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obtained was reduced in a hydrogen stream at 450°C for 2 h and cooled in a nitrogen atmosphere.

The hydrogenation reaction of rosin was carried out in a 300 ml autoclave. The reactor was charged with 30 g of rosin as a reactant, 3 g of catalyst, and 57 g of diethylene glycol dimethyl ether as a solvent. The hydrogenation reaction of rosin was performed at 260°C under 100 kg/cm^2 of H$_2$ for 6 h.

After the catalyst had been filtered off, the solvent was removed by vacuum distillation, then the remaining reaction products were analyzed on the basis of the acid value and the hydroxyl value. These values defined in the Japanese Industrial Standard, K0070 (1966).

We have prepared Ru–Sn catalysts by a conventional impregnation method using various tin compounds to hydrogenate rosin. Results are shown in Table 1. The Ru–Sn/alumina catalyst prepared from (Bu$_3$Sn)$_2$O gave a high yield of rosin alcohol (80%) on the hydrogenation of rosin (Table 1, Run 1).

Unfortunately, organic tin compounds are highly toxic; thus they are not suitable for industrial use. We tried inorganic tin compounds as nontoxic alternatives. Though SnCl$_2$ showed very little yield (22%, Run 2), the catalysts prepared from tin octoate, K$_2$SnO$_3$ and Na$_2$SnO$_3$ showed higher yield than the catalyst prepared from SnCl$_2$. The yield of rosin alcohol
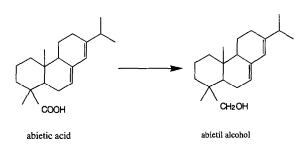
Table 1
Effect of Sn compound on yield of rosin alcohol [a]

Run	Sn compound	Yield of rosin alcohol [b](%)
1	(Bu$_3$Sn)$_2$O	80
2	SnCl$_2$	22
3	tin octoate	68
4	K$_2$SnO$_3$	84
5	Na$_2$SnO$_3$	77

[a] Rosin (30 g)/catalyst (3 g)/diethylene glycol dimethyl ether (57 g) at 260°C under 100 kg/cm^2 of H$_2$ for 6 h.
[b] Detected by the hydroxyl value and the acid value.

decreased in the order K$_2$SnO$_3$ ⩾ Na$_2$SnO$_3$ > tin octoate ≫ SnCl$_2$. On the catalyst prepared from SnCl$_2$, Cl was detected by EDX analysis. On the other hand, no Cl was detected on the catalyst prepared from tin octoate, K$_2$SnO$_3$, and Na$_2$SnO$_3$. As is generally known, Cl can be a poison to noble metal catalysts on alumina. Chlorine would inhibit the hydrogenation activity of –C=O. The catalyst prepared from K$_2$SnO$_3$ and Na$_2$SnO$_3$ showed higher yields than the catalyst prepared from tin octoate. In the catalyst prepared from K$_2$SnO$_3$ and Na$_2$SnO$_3$, K and Na were detected by EDX analysis, respectively.

On the other hand in the catalyst prepared from tin octoate, no alkaline metal was detected. The alkaline metal might affect the hydrogenation activity of –C=O. The effective materials were K$_2$SnO$_3$ and Na$_2$SnO$_3$ for the hydrogenation of –C=O, which can be prepared catalyst in industrial use.

Fig. 1. The hydrogenation of abietic acid, the major component of rosin, to its alcohol.

References

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