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Liquid-phase hydrogenation of dicarboxylates catalyzed by supported Ru–Sn catalysts

Katsuhiko Tahara [a,*], Hiroshi Tsuji [a], Hiroshi Kimura [a], Takumi Okazaki [a], Yasushi Itoi [a], Satoru Nishiyama [b], Shigeru Tsuruya [b], Mitsuo Masai [b]

[a] *Research Department, Arakawa Chemical Industries, Ltd., 1-1-9, Tsurumi, Tsurumi, Osaka 538, Japan*
[b] *Department of Chemical Science and Engineering, Kobe University, Rokkodai, Nada, Kobe 657, Japan*

Abstract

Heterogeneous Ru–Sn catalysts are effective for the liquid-phase hydrogenation of the C=O group in carboxylates: $(Bu_3Sn)_2O$ and $Sn(OEt)_4$ were used as Sn precursors, and Al_2O_3 and TiO_2 were found to be the appropriate supports. A catalyst made from $SnCl_2$ showed low activity for the hydrogenation of 1,4-cyclohexanedicarboxylic acid dimethyl ester, but its activity was increased by raising the calcination temperature, which served to remove Cl from the catalyst. The highest activity was found for an Ru–Sn catalyst which was alkali-washed after calcination.

Keywords: Liquid-phase hydrogenation of dicarboxylates; Ru–Sn catalysts

1. Introduction

The hydrogenation of carboxylates to alcohols is an important industrial process. Fatty alcohols have been produced by the hydrogenation of fatty acid esters using copper chromite catalysts under high pressure and temperature. Fatty alcohols, especially dialcohols, are industrially useful starting materials for polyurethane and polyester. In hydrogenation of dicarboxylates, low yields of dialcohols are produced by a concurrent transesterification reaction. Several bimetallic catalyst systems for the hydrogenation of carboxylates or carboxylic acids to corresponding alcohols have been reported. Narashimhan et al. [1,2] reported that methyl oleate was selectively hydrogenated to oleyl alcohol at a pressure of 44 kg/cm^2 and a temperature of 270°C by using Ru–Sn catalysts. Basset et al. [3,4] showed that ethyl acetate was hydrogenated to ethanol at a pressure of 100 kg/cm^2 and a temperature of 280°C by supported Rh–Sn catalysts prepared from organic metals. Mizukami et al. [5] reported the hydrogenation of oleic acid to 9-octadecen-1-ol at a pressure of 56 kg/cm^2 and a temperature of 240°C by Ru–Sn catalyst prepared by the sol–gel method. The sol–gel method by Mizukami [5] and the method using organometallic compounds by Basset [3,4] are not readily feasible for practical applications to industrial processes. We have studied the hydrogenation of carboxylates to the corresponding alcohols at an industrial level. Thus we reported the hydrogenation of dicarboxylates by Rh–Sn catalysts prepared

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[*] Corresponding author.

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by a more practical impregnation method [6]. It is our purpose to hydrogenate carboxylates to the corresponding alcohols on an industrial scale. Here, we report the hydrogenation of 1,4-cyclohexanedicarboxylic acid dimethyl ester (CHDC) and some other carboxylates to the corresponding alcohols using Ru–Sn catalysts prepared by the impregnation method in liquid phase (Fig. 1).

2. Experimental

2.1. Reagents

A ruthenium nitrosyl nitrate ($Ru(NO)(NO_3)_3$) solution (containing 5% Ru) was purchased from N.E. Chemcat, $SnCl_2 \cdot 2H_2O$ from Wako, $(Bu_3Sn)_2O$ from Tokyo Kasei Kogyo, $Sn(OEt)_4$ from E. Merck, alumina (Neobead GB, 220 m^2/g, 0.58 ml/g) from Mizusawa Industrial Chemicals, titania (MC-90) from Ishihara Sangyo Kaisha, silica–alumina (kyowaad 700) and magnesia (kyowamag and micromag) from Kyowa Chemical Industry, and zirconia from Nippon Shokubai. Methyl laurate and methyl benzoate were purchased from Tokyo Kasei Kogyo. Methyl iso-butylate, methyl oleate, methyl cyclohexane carboxylate, and CHDC were purchased from Wako.

2.2. Preparation of 5 wt.% Ru–11.7% Sn/alumina

Fifteen grams of alumina was soaked in an aqueous solution of $SnCl_2 \cdot 2H_2O$ (6 g of $SnCl_2 \cdot 2H_2O$ in 60 ml of water). The mixture was aged for 12 h at room temperature and dried at 70°C in a vacuum. The powder obtained was calcined at 400°C in an air stream for 2 h and washed with a 0.1 N/NaOH solution and dried at 70°C in a vacuum. Then 18 g of this powder was soaked in an 2-propanol solution of $Ru(NO)(NO_3)_3$ (17.05 g of $Ru(NO)(NO_3)_3$ solution in 60 ml of 2-propanol). The mixture was aged for 12 h at room temperature, and dried at 70°C in a vacuum. The powder obtained was reduced in a hydrogen stream at 450°C for 2 h and cooled in a nitrogen atmosphere.

2.3. Hydrogenation reaction

The hydrogenation reaction was carried out in a stainless-steel autoclave equipped with a mechanical stirrer (volume: 200 ml). The reactor was charged with 30 g of 1,4-cyclohexanedicarboxylic acid dimethyl ester as a reactant, 3 g of catalyst, and 57 g of diethylene glycol dimethyl ether as a solvent. After purging with hydrogen at 10 kg/cm^2 three times, the reactor was pressurized with H_2 to 60

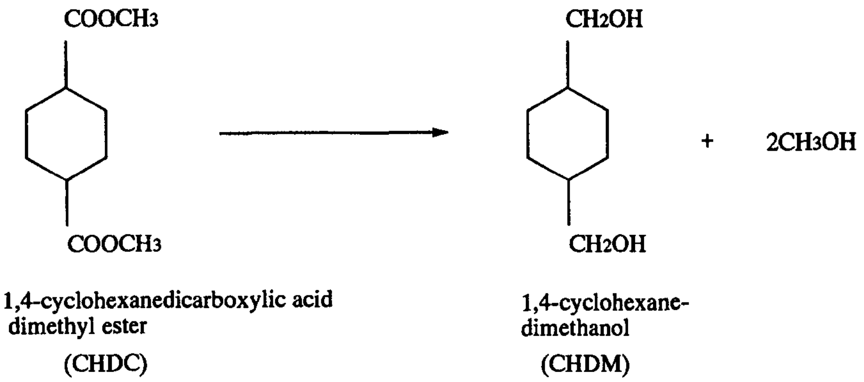

Fig. 1. Hydrogenation of 1,4-cyclohexane dicarboxylic acid dimethylesther (CHDC).

kg/cm^2. The reactor was then heated up to 280°C for 30 min and was then pressurized with H_2 to 100 kg/cm^2. The reaction was performed at 280°C under 100 kg/cm^2 of H_2 for 6 h. The reactor was cooled down to room temperature, then the reaction mixture was recovered for analysis.

2.4. Analysis of hydrogenation products

After the catalyst was filtered off, the solvent was removed by vacuum distillation. Finally, the remaining reaction products were analyzed by a gas chromatograph equipped with a 30-m 0.32-mm capillary column (DB-WAX).

2.5. Gas adsorption and removal of Cl from catalysts

The amount of removed Cl was measured by EDX as follows: when the catalyst was prepared from $SnCl_2$ without calcination, the height ratio of Cl/Al was assumed to 1. Adsorption of CO was measured at −80°C by the pulse flow method. H_2 adsorption was measured at room temperature by a static method.

3. Results and discussion

3.1. Effect of starting material of Sn on CHDM yield

The main reaction pathway was shown in Fig. 1. Only 1,4-cyclohexanedimethanol (CHDM) and methanol were observed as products. We have prepared the Ru–Sn catalysts, without calcination using various tin compounds (Table 1). The Ru-Sn/alumina catalyst prepared from $Sn(OEt)_4$ and $(Bu_3Sn)_2O$ gave CHDM a high yield (run 1,2). The Ru–Sn/titania catalyst prepared from $(Bu_3Sn)_2O$ resulted in a higher yield of CHDM than the Ru–Sn/alumina catalyst (run 3). Unfortunately, organic tin compounds have strong toxicity, thus they are not suitable for industrial use. We tried an inorganic tin compound as a nontoxic compound, but $SnCl_2$ gave a very poor CHDM yield (run 4,5).

Table 1
Effect of starting material of Sn on the yield of CHDM [a]

Run no.	Sn compound	Supports	CHDM yield (%)
1 [b]	$Sn(OEt)_4$	Al_2O_3	72
2 [c]	$(Bu_3Sn)_2O$	Al_2O_3	75
3 [c]	$(Bu_3Sn)_2O$	TiO_2	85
4 [b]	$SnCl_2$	Al_2O_3	0
5 [b]	$SnCl_2$	TiO_2	0

[a] The catalysts were prepared without calcination.
[b] Tin metal loading was 11.7 wt.%. [c] Tin metal loading was 23.4 wt.%.

As generally known, Cl can be a poison to the noble metal catalysts on alumina. The presence of Cl inhibited the hydrogenation of C=O in our work with the Ru–Sn catalyst which was prepared from $SnCl_2$. On the other hand, with the Ru–Sn catalyst prepared from organic tin compounds, the absence of Cl made the CHDM yield high. Nishiyama et al. [7] have studied the selective hydrogenation of crotonaldehyde with Rh–Sn catalysts and have found that the tin reduced to a low-valence state on the catalyst surface was effective for the hydrogenation of the C=O group. In the Ru–Sn catalyst which was prepared from $SnCl_2$, Sn was not reduced to low-valence state because of the presence of Cl. On the other hand, in the Ru–Sn catalyst prepared from organic tin compounds, the absence of Cl made the reduction of tin to low-valence state much simpler and made the CHDM yield high.

3.2. Effect of calcination and washing on Ru–Sn / alumina catalyst prepared from $SnCl_2$ on CHDM yield

To improve the activity of the Ru–Sn catalysts prepared from $SnCl_2 \cdot 2H_2O$, the effect of calcination followed by washing of the catalysts was investigated as shown in Table 2. The calcination of the Ru–Sn/alumina catalysts at 400 or 600°C was effective for the CHDM

Table 2
Effect of calcination with washing on Ru–Sn/alumina catalyst [a]

Run no.	Calcination temperature (°C)	CHDM yield (%)	Removed Cl (%)
1	none	0	0
2	400	56	85
3	600	57	87
4	800	29	100
5	400 and wash	78	100

[a] The catalysts were prepared from $SnCl_2$ and alumina.

yield, but the Ru–Sn catalyst calcined at 800°C showed a lower CHDM yield. However, the Ru–Sn catalyst washed after calcination at 400°C resulted in the highest CHDM yield. Almost 85% of Cl over the Ru–Sn catalyst was removed by calcination at 400°C and 600°C. The Ru–Sn catalysts after the calcination at 400°C and 600°C indicated ca. 57% of the CHDM yield. The absence of Cl made the CHDM yield high. On the other hand, in the Ru–Sn catalyst calcined at 800°C, most of the Cl was removed but the CHDM yield became low.

Table 3 shows the results of carbon monoxide (CO) and hydrogen (H_2) chemisorption studies of the calcined and washed catalysts. It is generally known that CO and H_2 are not chemisorbed on the Sn and alumina surfaces irreversibly. In this catalyst system, CO and H_2 can be chemisorbed on the Ru surface. In the Ru–Sn catalyst calcined at 800°C, the amount of CO and H_2 adsorption was greater than those at 600°C and 400°C. The high value of adsorption capacity does not only mean decrease of particle size but also shows separation of Ru and Sn in the catalyst. In the Ru–Sn catalyst calcined at 800°C, most of the Cl was removed but on the catalyst surface Ru and Sn were separated to result in both a high adsorption capacity and a low CHDM yield. On the other hand, in the Ru–Sn catalyst washed after calcination at 400°C, most of the Cl was removed although the surface Ru and Sn were not separated. As a result, the adsorption capacity stayed low and the CHDM yield was the highest. The removed Cl and Ru–Sn alloy may be important for the hydrogenation activity of CHDC.

Table 3
Gas adsorption of the Ru–Sn/alumina catalyst [a]

Run no.	Calcination temperature (°C)	Adsorption (ml/$g_{cat.}$)	
		CO	H_2
1	none	0.05	0.05
2	400	0.05	0.05
3	600	1.00	0.50
4	800	4.00	1.00
5	400 and wash	1.30	0.30

[a] The catalysts were prepared from $SnCl_2$ and alumina.

Table 4
Effect of supports on the Ru–Sn catalyst [a]

Run no.	Supports	CHDM yield (%)
1	alumina (neobead GB)	78
2	silica–alumina (kyowaad 700)	46
3	zirconia	25
4	magnesia (micromag)	22
5	magnesia (kyowamag)	31
6 [b]	titania (MC-90)	85

[a] The catalysts were prepared from $SnCl_2$ with washing after calcination.

[b] The catalysts were prepared from $(Bu_3Sn)_2O$ without calcination.

3.3. *Effect of supports on the Ru–Sn catalysts*

We have investigated the effect of supports of the Ru–Sn catalyst prepared by the impregnation method on the hydrogenation of CHDC. Results are shown in Table 4. The CHDM yield over the alumina-supported catalyst was 78% (run 1) and that over the silica–alumina-supported catalyst was 46% (run 2). The CHDM yield over the ZrO_2-supported catalyst was 25% (run 3) and MgO-supported catalysts were 22 and 31%, respectively (run 4, 5). We have previously reported the effect of support on the Rh–Sn catalyst in the hydrogenation of dicarboxylates (methyl oleate dimmer) [6]. Alumina and titania were effective carriers. Mizukami et al. [5] studied the effect of support of the Ru–Sn catalyst prepared by the sol–gel method on the hydrogenation of oleic acid. The activity of a

Table 5
Hydrogenation of various carboxylates on Ru–Sn/alumina catalyst

Run no.	Substrate	Product	Conversion (%)	Selectivity (%)
1	methyl laurate	lauryl alcohol	99	96
2	methyl cyclohexane-carboxylate	cyclohexane methanol	99	96
3	methyl iso-butylate	iso-butylalcohol	60	98
4	methyl oleate	stearyl alcohol	98	98
5	methyl benzoate	benzyl alcohol	99	18
		cyclohexyl methanol		49
		toluene		32

The catalysts were prepared from $SnCl_2$ and alumina.

supported catalyst decreased in the order alumina > zirconia > silica > titania. The alumina and titania were effective supports for the hydrogenation of CHDC using the Ru–Sn catalyst prepared by the impregnation method.

3.4. Hydrogenation of various carboxylates on Ru–Sn / alumina catalyst

The hydrogenation of various carboxylates over the Ru–Sn/alumina was also carried out. The results are shown in Table 5. The catalyst showed higher activity in the hydrogenation of methyl laurate (run 1) and methyl cyclohexanecarboxylate (run 2) than in the hydrogenation of methyl isobutylate (run 4).

The catalysts showed higher activity in the hydrogenation of methyl oleate, and the product was stearyl alcohol. Methyl benzoate was hydrogenated to benzyl alcohol and cyclohexanemethanol on the Ru–Sn catalysts. On Ru/alumina catalysts, cyclohexanemethanol and toluene were mainly produced. Mizukami et al. [5] reported the hydrogenation of oleic acid on the sol–gel Ru–Sn catalyst which can preserve the double bond, thus the product was 9-octadecen-1-ol. The catalyst prepared in our work adsorbed more CO (1.3 ml/g cat.) than the catalyst prepared by the sol–gel method (no adsorption of CO). As described in Section 3.2, high CO and H_2 adsorption capacity results in separated Ru particles. In our present work, it seems that the surface Ru is left intact and that the separated Ru particles can hydrogenate the C=C bond and benzene ring. On the Ru particles, benzyl alcohol was hydrogenated to toluene.

4. Conclusions

(1) The Ru–Sn bimetallic system is an effective catalyst for selective hydrogenation of the C=O group in carboxylates.

(2) The type of tin compound for the preparation of the bimetallic catalysts plays a significant role in hydrogenation activity. The most effective materials are $(Bu_3Sn)_2O$ and $Sn(OEt)_4$.

(3) Although the Ru–Sn catalyst prepared from $SnCl_2$ shows low activity without calcination, the C=O hydrogenation activity increases with an increase of calcination temperature.

(4) Calcination and washing in the catalyst preparation also markedly affect the activity.

(5) Alumina is the best support among those studied here.

(6) The Ru–Sn catalyst washed after calcination is effective for the hydrogenation of various carboxylates.

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