Catalysis Letters 30 (1995) 297–304

Selective hydrogenation of ethyl phenylacetate to 2-phenylethanol: a convenient catalyst preparation method

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Received 8 August 1994; accepted 17 October 1994

A ruthenium–tin–alumina catalyst, prepared by a combination of kneading and impregnation methods, which we have named the combination method, was able to selectively hydrogenate ethyl phenylacetate to 2-phenylethanol; tin oxide was used as a chloride-free tin source. For this combination catalyst, the optimum atomic ratio for Ru : Sn was found to be 1 : 4. X-ray diffraction measurements showed the presence of tin particles. It appeared that the number of the tin particles had a large effect on the hydrogenation of C=O groups. However, the catalyst prepared with ruthenium oxide had a low activity, possibly owing to the ruthenium metal or ruthenium–tin alloy, which was formed and which obstructed the reaction.

Keywords: hydrogenation; ruthenium/tin/alumina; combination; sol–gel; impregnation; ethyl phenylacetate; 2-phenylethanol

1. Introduction

Hydrogenation of fatty and aromatic acids, or their esters, to corresponding alcohols is an important industrial process. Consequently, many investigations regarding such processes have been undertaken [1–15].

Recently, we investigated the selective hydrogenation of carboxylic acids, or their respective esters, to the corresponding unsaturated alcohols by use of ruthenium–tin–alumina catalysts maintained at low pressure [14]. A catalyst prepared by an improved sol–gel method selectively hydrogenated oleic acid to 9-octadecen-1-ol. However, this preparation method was rather complicated, also requiring an expensive metal alkoxide reagent. We also found that a catalyst prepared by an impregnation method yielded the best results for selective hydrogena-

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tion of ethyl phenylacetate to 2-phenylethanol [15]. The main problem concerning this method was the requirement for soluble chloride-free metal raw materials. Tin oxide is the most convenient form from which to obtain a chloride-free tin source, however, its insolubility in any solvent means that kneading is the only method which results in the alumina support containing the oxide.

In the present paper, we report the development of another preparation method to overcome these problems: a combination of kneading and impregnation, using tin oxide as the chloride-free tin source. This catalyst also hydrogenated ethyl phenylacetate to 2-phenylethanol with a high yield.

2. Experimental

Tris(acetylacetonato)ruthenium(III) ($Ru(acac)_3$) was converted into the corresponding nitrate by treatment at ca. 353 K with nitric acid, prior to the catalyst preparation.

Preparation of chloride-free ruthenium solution. Sixty grams of concentrated nitric acid was carefully added to 2.96 g of $Ru(acac)_3$ and the mixture was stirred for 14 h at 353 K. During the first 10 min, nitrogen oxide was generated, and after 14 h the solution had become clear and red. The solution was then evaporated and 20 cm^3 of ethanol was added.

Combination of kneading and impregnation method (combination method). The ruthenium–tin supported catalysts were prepared by the following combination method; $Ru(acac)_3$ and tin oxide were used as the raw materials, and high purity alumina of Ketjen was used as the support for the catalysts. Tin oxide (2.24 g) and alumina (12.5 g) were kneaded mechanically with a small amount of distilled water for 30 min using an agate mortar. A study of the effect of the kneading time on the catalyst performance has not been conducted. This mixed paste was dried in a dry oven at 385 K overnight. After drying, the ruthenium solution stated above was impregnated onto the dried tin–alumina at room temperature for approximately 12 h, and then the ethanol was removed in vacuo at 353 K. Finally, the catalyst was obtained after activation in an atmosphere of hydrogen at 673 K for 4 h.

Complexing agent-assisted sol–gel (chemical mixing) method [17]. $Ru(acac)_3$ and tin *n*-butoxide [$Sn(OBu^n)_4$] were used as the raw materials and 2-methyl-2,4-pentanediol was used as the solvent. This catalyst was prepared as follows: 56 g of aluminum isopropoxide [$Al(OPr^i)_3$] and 130 g of 2-methyl-2,4-pentanediol were mixed at room temperature and then heated to 393 K whilst stirring. After having completely dissolved, the isopropanol, which had been produced by a ligand-exchange reaction, was removed in vacuo at 353 K. The ruthenium solution, which had been prepared beforehand, and 4.7 g of $Sn(OBu^n)_4$ were then added and the mixture was stirred for 2 h at 353 K. The ethanol and the butanol were then removed in vacuo at the same temperature. This second solution was added to the mixed solution, which had been prepared from 90 g of water and 60 g of 2-methyl-2,4-pentanediol. The viscous solution which was obtained, was aged over night at room temperature before being dried at 423 K in vacuo.

Conventional impregnation method. High purity alumina of Ketjen was used as the support for the catalysts. Ru(acac)$_3$ and Sn(OBu^n)$_4$ were used as the raw materials. The impregnation of the ruthenium and tin onto the support was undertaken in the conventional manner using ethanol as the solvent.

Conventional kneading method. High purity alumina of Ketjen was used as the support for the catalysts. RuO_2 and SnO_2 were used as the raw materials. The kneading of the ruthenium and tin with the support was carried out in the conventional manner with a small amount of water.

Hydrogenation reaction. The hydrogenation reaction was undertaken in a 200 dm^3 reactor equipped with a pressure regulator. The reactor was charged with ethyl phenylacetate, together with the catalyst, and purged with hydrogen four times at different pressures (1.0, 1.0, 2.0 and 4.0 MPa) to remove the air. The reactor was then heated to the required temperature and pressurized with hydrogen to the reaction pressure. The speed of the stirrer used to mix the solution was maintained at 1500 rpm. After 15 h, the reactor was allowed to cool and the reaction mixture was recovered for analysis.

Analysis of products. The reaction products were analyzed by gas chromatography with a 1 m x 3 mm column (Shinwa-kako Co. Ltd., support: shincarbon A, liquid phase: thermon 3000). A flame ionization detector was used and the carrier gas was nitrogen.

Characterisation of catalysts. The solids were characterised with a MAC Science MXP-18 X-ray diffractometer, using Ni filtered Cu K$_\alpha$ radiation.

3. Results and discussion

3.1. EFFECT OF CATALYST PREPARATION METHOD

Table 1 shows the effect of the catalyst preparation method on the activity and selectivity of the Ru/Sn/Al_2O_3 catalyst for the hydrogenation of ethyl phenylacetate. Catalysts with the same composition were prepared from chloride-free raw materials. For all the catalysts, the activities, in terms of conversion, were comparable, and were not affected by the preparation method. However, with regard to the selectivity of 2-phenylethanol, the combination catalyst was slightly inferior, although, it appeared that tin oxide was a useful source of tin in the catalyst.

X-ray diffraction patterns of the catalysts after activation are shown in fig. 1. It was not possible to observe a crystalline phase of the ruthenium metal for any of the catalysts, suggesting that the ruthenium metal was dispersed on the support. For the sol–gel and the impregnation catalysts, only the diffraction maxima corresponding to the γ-alumina phase were observed. In contrast to this, the combina-

Table 1
Effect of catalyst preparation method on the catalytic activity and selectivity in the hydrogenation of ethyl phenylacetate[a]

Preparation method	Conversion (%)	Selectivity (%)
combination	93.2	81.9
sol–gel	88.4	93.3
impregnation	91.9	94.9

[a] Experimental conditions were as follows: All catalysts were prepared using $Ru(acac)_3$, which was converted into the corresponding nitrate by treatment at ca. 353 K with nitric acid prior to the catalyst preparation. The combination catalyst was prepared using tin oxide as a tin source, in contrast to the sol–gel and impregnation catalysts which were prepared using $Sn(OBu^n)_4$ as the tin source. For all the catalysts, the ruthenium metal loading was 5 wt% and the atomic ratio of Ru : Sn was 1 : 2. The catalysts were activated in a hydrogen stream at 673 K for 4 h. Reaction conditions: temperature, 513 K; pressure, 8 MPa; reaction time, 15 h; ethyl phenylacetate, 80 g, and catalyst, 5% by weight.

tion catalyst had a high yield of tin in the metal phase. Thus, the different X-ray diffraction patterns were related to the presence or absence of tin particles in the catalysts. The different size of the tin particles for the same compositions of the ruthenium and the tin indicates the different dispersion state of the tin. For the sol–gel and the impregnation catalysts, the tin was well dispersed on the support because these catalysts were prepared from an ethanol solution of the tin. For the combination catalyst, however, which was prepared from a solid state support and

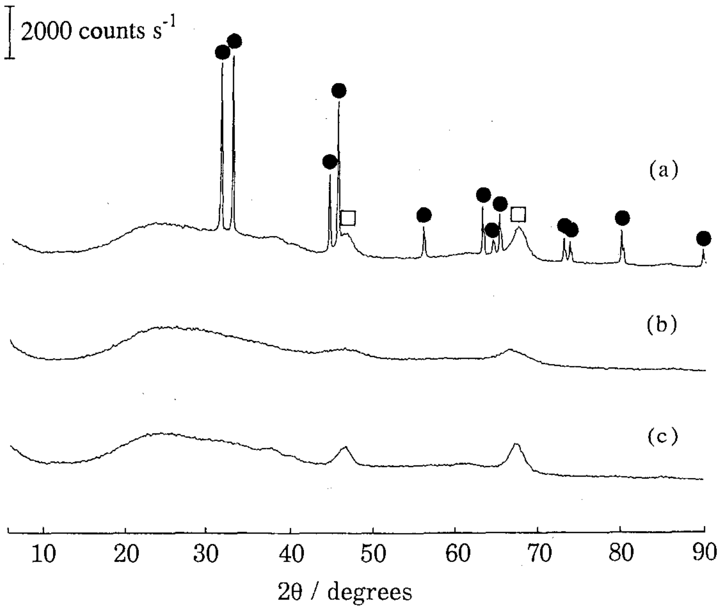

Fig. 1. X-ray diffraction patterns of catalysts prepared by different methods. (a) Combination; (b) sol–gel; (c) impregnation. (□) γ-alumina; (●) Sn metal.

tin oxide, dispersion of the tin was lower, owing to the larger size of the tin particles compared with those of the corresponding sol–gel and impregnation catalysts. Thus, there was insufficient tin in close proximity to the ruthenium for the reaction to occur. Consequently, the selectivity to 2-phenylethanol was decreased by the active ruthenium, which was not able to interact with any tin.

3.2. EFFECT OF THE ATOMIC RATIO OF RUTHENIUM TO TIN IN THE COMBINATION CATALYSTS

Table 2 shows the effect of the atomic ratio of ruthenium to tin in the combination catalysts on the catalytic activity and selectivity of 2-phenylethanol formation in the hydrogenation of ethyl phenylacetate. We had already determined that the Ru/Al_2O_3 catalyst, which did not contain tin, had a high activity, but poor selectivity for 2-phenylethanol. Mostly saturated products were obtained, the others being mainly hydrocarbons. 5 wt% $Ru/2.94$ wt% Sn/Al_2O_3 catalyst ($Sn/Ru = 0.5$) also yielded only saturated products. However, when tin was added to increase the Sn/Ru ratio to 1, 2 or 4, the selectivity of 2-phenylethanol increased, but for a Sn/Ru ratio greater than 4, no further increase was observed. A Ru : Sn atomic ratio of 1 : 4 seemed to be optimum for selective hydrogenation of ethyl phenylacetate to 2-phenylethanol as it resulted in about 93.5% selectivity of unsaturated alcohol, and a conversion rate of 89.0%. It appeared that the tin had a large influence on the hydrogenation of C=O groups though preserving the aromatic rings, and a high selectivity was obtained when the Sn/Ru ratio was greater than or equal to 4. Fig. 2 shows typical X-ray diffraction patterns of four samples ($Sn/Ru = 1, 2, 4, 8$) after activation. On increasing the tin ratio, the relative intensity of the tin metal phase became stronger, indicating a corresponding increase of tin particles, which had a large effect on the selectivity. It was also noted that both the tin oxide phase, which was not reduced by activation, and the tin metal phase were observed on the X-ray diffraction pattern for $Sn/Ru = 8$. For a Sn/Ru ratio greater than 4, the catalytic activity decreased, possibly owing to the presence of both of the remaining tin species, viz. tin oxide and the excess tin. Although this had no effect on the reaction, it prevented the ruthenium contacting the substrate, and thereby caused the observed decrease of the reaction rate.

Table 2
Effect of the atomic ratio of ruthenium to tin in the combination catalysts on the hydrogenation of ethyl phenylacetate[a]

Catalyst	Sn/Ru	Conversion (%)	Selectivity (%)
5 wt% $Ru/2.94$ wt% Sn/Al_2O_3	0.5	100	0
5 wt% $Ru/5.88$ wt% Sn/Al_2O_3	1	86.7	77.4
5 wt% $Ru/11.75$ wt% Sn/Al_2O_3	2	93.2	81.9
5 wt% $Ru/23.5$ wt% Sn/Al_2O_3	4	89.0	93.7
5 wt% $Ru/47$ wt% Sn/Al_2O_3	8	58.0	95.0

[a] For reaction conditions see table 1.

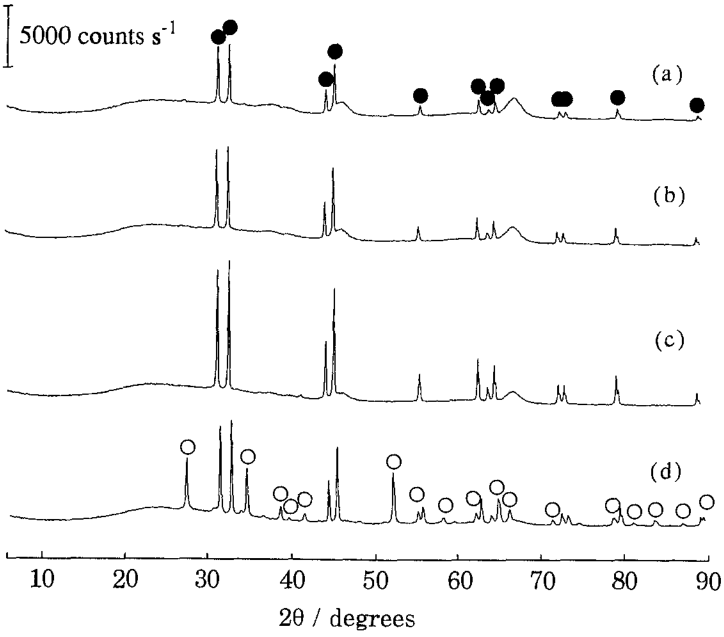

Fig. 2. Effect of the atomic ratio of ruthenium to tin in the combination catalysts on X-ray diffraction patterns. (a) Sn/Ru = 1; (b) Sn/Ru = 2; (c) Sn/Ru = 4; (d) Sn/Ru = 8. (●) Sn metal; (○) SnO_2.

3.3. EFFECT OF RUTHENIUM SOURCE IN THE COMBINATION CATALYSTS

Table 3 shows the effect of different ruthenium source materials in the combination catalysts, on the activity and selectivity in the hydrogenation of ethyl phenylacetate to 2-phenylethanol. Catalysts with the same composition were prepared for 5 wt% Ru/23.5 wt% Sn/Al_2O_3. For both the RuO_2 catalysts, the conversion rate was relatively low, being lowest for the catalyst activated for 8 h at 873 K. Fig. 3 shows the X-ray diffraction patterns after activation. Under ordinary activation conditions (673 K for 4 h), the Ru metal phase resulting from the RuO_2 was observed. However, under the severe activation conditions (873 K for 4 h), the Ru–Sn alloy phase appeared, suggesting that both the Ru metal and Ru–Sn alloy, which had crystalline particles of sufficient size to diffract X-rays, were the cause of

Table 3
Effect of ruthenium source on the hydrogenation of ethyl phenylacetate[a]

Ru source	Activation condition	Conversion (%)	Selectivity (%)
$Ru(acac)_3$	673 K, 4 h	89.0	93.7
RuO_2	673 K, 4 h	14.9	92.1
RuO_2	873 K, 8 h	10.2	98.0

[a] Ruthenium metal loading was 5 wt% and the atomic ratio of Ru : Sn was 1 : 4. For reaction conditions see table 1.

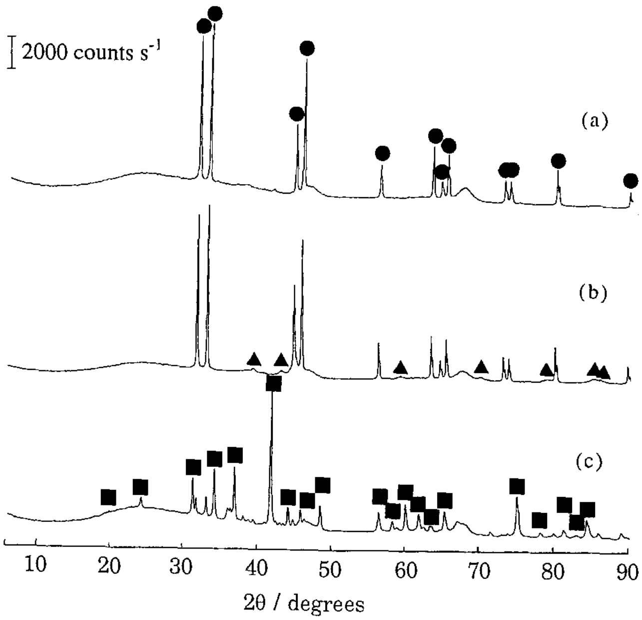

Fig. 3. Effect of ruthenium source in the combination catalysts on X-ray diffraction patterns. (a) $Ru(acac)_3$, activation conditions: 673 K, 4 h; (b) RuO_2, activation conditions: 673 K, 4 h; (c) RuO_2, activation conditions: 873 K, 8 h. (●) Sn metal: (▲) Ru metal; (■) Ru–Sn alloy.

the activity decrease and were therefore not suitable for the catalytic reaction. Thus, this catalyst system requires dispersion of the ruthenium. For the catalyst, which was formed from ruthenium metal particles, the selectivity and conversion were also both low. It is possible that the selectivity decreased owing to the active area of the ruthenium metal particles which did not interact with the tin, and the conversion rate also decreased with the decrease in the number of reaction sites. Moreover, it seemed that the formation of Ru–Sn alloy particles obstructed the catalytic reaction to a larger extent than did the Ru metal particles.

4. Conclusions

A $Ru/Sn/Al_2O_3$ catalyst, prepared by a novel combination method using tin oxide as a chloride-free source, was able to selectively hydrogenate ethyl phenylacetate to 2-phenylethanol. This result suggests that such a combination method is a suitable and convenient procedure for such reactions.

Acknowledgement

We would like to express our thanks to Dr. Mark J. Jeffery (ETL) and Dr. Hirobumi Ushijima (NIMC) for valuable discussions.

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