Effects of Raw Materials and Preparation Methods of Catalysts on the Selective Hydrogenation of Ethyl Phenylacetate

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ABSTRACT: A ruthenium/tin/alumina catalyst was found to hydrogenate ethyl phenylacetate to 2-phenylethanol selectively with a high yield. The optimum atomic ratio of ruthenium to tin was 1:2, and the optimum metal content was about 5 and 11.75 wt% for ruthenium and tin, respectively. The raw materials of the catalyst had a significant effect on the conversion and selectivity in the catalytic hydrogenation. Chloride had a negative effect on catalytic activity. Washing the catalysts, which were prepared from chloride materials, with distilled water or alkali solution had a positive effect upon catalyst activity. The catalyst prepared from chloride-free raw materials performed the best, and the impregnation catalyst has a higher yield than the sol-gel catalyst, suggesting that impregnation is a suitable procedure for this reaction.

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KEY WORDS: Ethyl-phenylacetate, hydrogenation, impregnation, 2-phenylethanol, ruthenium/tin/alumina, sol-gel.

Hydrogenation of fatty and aromatic acids, or their esters, to corresponding alcohols is an important industrial process which is currently carried out under high pressure (20–30 MPa) and high temperature (523–573 K). Several attempts have been made to develop suitable catalysts that can hydrogenate acids or esters to respective alcohols under mild conditions (1–4). We have previously reported the development of a new ruthenium/tin/alumina catalyst, prepared by an improved sol-gel method, which selectively hydrogenate oleic acid to 9-octadecene-1-ol at low pressure (5.6 MPa) and 523 K (5). We also found that a rhenium/tin catalyst could hydrogenate oleic acid to 9-octadecene-1-ol (6). Both of these previous results suggested that catalyst preparation and the raw materials used have a large effect on the catalytic properties. It is well known that remaining chloride ions on a noble metal catalyst have a large negative effect. For ruthenium catalysts, the negative effect is relatively large due to the fact that removing chloride ions from the ruthenium catalyst is more difficult than from other noble metal catalysts (7–9). This negative effect is a reason for using some expensive raw materials instead of lower-cost chloride-based materials.

We report here an investigation into selective hydrogenation of ethyl phenylacetate to 2-phenylethanol with a ruthenium/tin/alumina catalyst system, which was found to hydrogenate ethyl phenylacetate to 2-phenylethanol with a high yield. We also undertook a detailed investigation into the effect of the raw materials used and compared this with the performance of the catalysts prepared by sol-gel and impregnation methods.

EXPERIMENTAL PROCEDURES

Materials. Bis(acetylacetonato)tin(II), $[Sn(acac)_2]$, used as a chloride-free tin source was purchased from Kawaken Fine Chemicals Co., Ltd. (Kawagoe, Saitama, Japan). Other chemicals were guaranteed reagent grade unless otherwise stated.

Catalyst preparation. Tris(acetylacetonato)ruthenium(III), $[Ru(acac)_3]$, was converted into the corresponding nitrate by treatment at *ca.* 35 K with nitric acid prior to catalyst preparation.

Preparation of chloride-free ruthenium solution. Sixty grams of concentrated nitric acid was carefully added to 2.96 g $Ru(acac)_3$, 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.

Complexing agent-assisted sol-gel (chemical mixing) method (10). $Ru(acac)_3$ 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. The catalyst, which will be referred to as the sol-gel catalyst, was prepared as follows: 56 g aluminum isopropoxide, $[Al(OPr^i)_3]$, and 130 g 2-methyl-2,4-pentanediol were mixed at room temperature and then heated to 393 K while stirring. After having completely dissolved, the *iso*-propanol, which had been produced by a ligand-exchange reaction, was removed *in vacuo* at 353 K. The ruthenium solu-

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tion, which had been prepared beforehand, and 4.7 g $Sn(OBu^n)_4$ were then added, and the mixture was stirred for 2 h at 353 K. The ethanol and butanol were then removed, again *in vacuo*, at the same temperature. This second solution was added to the mixed solution which had been prepared from 90 g water and 60 g 2-methyl-2,4-pentanediol. The viscous solution was aged overnight at room temperature before being dried at 423 K *in vacuo*. Finally, the catalyst was obtained after activation in an atmosphere of hydrogen at 673 K for 4 h. Following the same procedure, a catalyst was prepared from ruthenium chloride hydrate ($RuCl_3 \cdot nH_2O$) and stannous chloride hydrate ($SnCl_2 \cdot 2H_2O$).

Conventional impregnation method. High-purity alumina of Ketjen was used as the support for these catalysts (referred to as the impregnation catalyst). $Ru(acac)_3$ and $Sn(OBu^n)_4$ were used as the raw materials. The impregnation of ruthenium and tin onto the support was undertaken in the conventional manner with ethanol as the solvent. Following the same procedure, a catalyst was prepared from $RuCl_3 \cdot nH_2O$ and $SnCl_2 \cdot 2H_2O$.

Removal of the chloride ions from the catalyst by washing: washing with distilled water. The catalyst, which was activated in a hydrogen atmosphere, was suspended in distilled water and stirred for 3 h. The suspended solution was then filtered, and the remaining solid was washed with distilled water until no precipitate of silver chloride (AgCl) formed upon addition of an aqueous solution of silver nitrate ($AgNO_3$ aq.) was observed.

Washing by KOH aqueous. The catalyst, which was activated in a hydrogen atmosphere was suspended in an aqueous solution of 0.1 mol cm^{-3} of potassium hydroxide (KOH aq.) and stirred for 3 h. Then the suspended solution was filtered, and the precipitate was washed with distilled water until the filtered solution became neutral.

Hydrogenation reaction. The hydrogenation reaction was undertaken in a 200-cm^3 reactor equipped with a pressure regulator. The reactor was charged with the 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 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 × 3 mm column (Shinwakako Co. Ltd., Kyoto, Japan; support: shincarbon A, liquid phase: thermon 3000) operated with temperature programming from 403 to 523 K at 2 K/min after holding at 403 K for 5 min. A flame-ionization detector was used, and the carrier gas was nitrogen. The retention times of ethyl phenylacetate and 2-phenylethanol were 14.7 and 18.9 min, respectively.

Characterization of catalysts. The solids that were activated in a hydrogen atmosphere were characterized by X-ray photoelectron spectra (XPS). XPS were acquired on a Shimadzu (Tokyo, Japan) ESCA-850 spectrophotometer with an Mg anode in a vacuum of 10^{-6} Pa. All measured binding energies were adjusted with respect to the evaporated Au $4f_{7/2}$ peak at 83.3 eV.

RESULTS AND DISCUSSION

Effect of the atomic ratio of ruthenium to tin. Table 1 shows the effect of the atomic ratio of ruthenium to tin in the sol-gel catalysts on the catalytic activity and selectivity of 2-phenylethanol formation in the hydrogenation of ethyl phenylacetate. The Ru/Al_2O_3 catalyst (Sn/Ru = 0) showed a high conversion rate (100%) but poor selectivity (0%) for 2-phenylethanol. Mostly saturated products were obtained, the others being mainly hydrocarbons. However,when tin was added to increase the Sn/Ru ratio to 1, the selectivity of 2-phenylethanol increased, but for a Sn/Ru ratio greater than 1, no further increase was observed. With regard to the conversion rate, when tin was added (Sn/Ru = 1), the rate decreased to 48.3%. For Sn/Ru ratios greater then 2, both conversion rate and selectivity were not improved much. An Ru/Sn atomic ratio of 1:2 seemed to be optimum for selective hydrogenation of ethyl phenylacetate to 2-phenylethanol. From the above results, it appeared that tin had a large influence on the hydrogenation of C=O groups while preserving the aromatic ring.

Effect of metal contents in the catalysts. Figure 1 shows the effect of metal contents in the sol-gel catalysts on the conversion and selectivity in the hydrogenation of ethyl phenylacetate. An Sn/Ru atomic ratio of 2 was used in all catalysts. On increasing the ruthenium content from 2 to 5 wt%, the conversion rate increased linearly, but increasing the ruthenium content further resulted in a slight decrease in the conversion rate. The selectivity, on the other hand, remained almost constant for all catalysts. Thus the optimum metal content was approximately 5 wt% Ru/11.75 wt% Sn, with no adverse effect if the ruthenium content exceeded 5 wt%.

Effect of the catalyst raw materials. It is well known that remaining chloride ions have a large effect on the catalytic reaction. Miura and co-workers (7–9) reported that the ability of hydrogen adsorption in the ruthenium catalysts was decreased because of remaining chloride ions, and that it is ex-

TABLE 1

Effect of Atomic Ratio of Ruthenium to Tin on the Catalytic Activity and Selectivity in the Hydrogenation of Ethyl Phenylacetate[a]

Catalyst	Sn/Ru (atomic ratio)	Conversion (%)	Selectivity (%)
2 wt% Ru/Al_2O_3	0	100	0
2 wt% Ru/2.35 wt% Sn/Al_2O_3	1	48.3	96.2
2 wt% Ru/4.7 wt% Sn/Al_2O_3	2	54.7	95.9
2 wt% Ru/9.4 wt% Sn/Al_2O_3	4	52.7	95.9

[a] Experimental conditions were as follows: The catalysts were prepared by a sol-gel method from $Ru(acac)_3$, $Sn(OBu^n)_4$, and $Al(OPr^i)_3$ with 2-methyl-2,4-pentanediol as the solvent. $Ru(acac)_3$ was converted into the corresponding nitrate by treatment with nitric acid at *ca.* 353 K prior to the sol-gel catalyst preparation. 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; catalyst, 5% by weight.

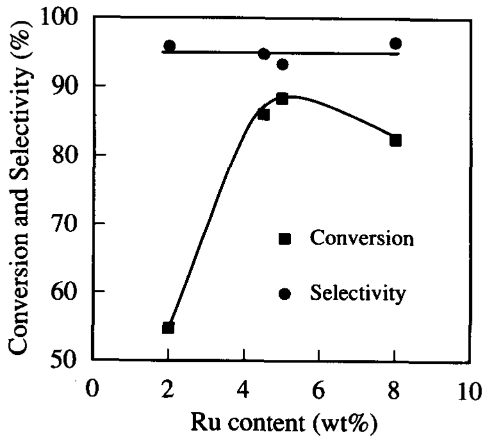

FIG. 1. Effect of metal content on conversion and selectivity in the hydrogenation of ethyl phenylacetate. The atomic ratio of Ru/Sn was always 1:2.

tremely difficult to remove the ions completely by calcination or reduction treatment. Table 2 shows the effect of the catalyst raw materials, in both sol-gel and impregnation catalysts, on the conversion rate and selectivity in the hydrogenation catalysts, prepared from metal chloride, and it is clear that the conversion rates were significantly lower than those for the corresponding catalysts prepared from a chloride-free metal source, suggesting that the remaining chloride ions inhibited the reaction.

Effect of washing on catalyst performance. We investigated the removal of chloride ions from the catalysts prepared with metal chloride. Table 3 shows the effect of washing on catalyst performance in the hydrogenation of ethyl phenylacetate.

Washing with distilled water. We had already checked the removal of chloride ions from the catalyst by precipitation of AgCl, which was formed by adding $AgNO_3$ aq. to the filtered water after washing the catalyst. For the sol-gel catalyst washed with distilled water, the conversion rate increased only slightly; however, that of the impregnation catalyst increased greatly, from 41.4 to 72.7%. It appeared that washing with distilled water had a positive effect, especially for the impregnation catalyst.

Washing by KOH aq. The conversion rate of the impregnation catalyst washed with KOH aq. was essentially the same as that of the impregnation catalyst washed with distilled water. For the impregnation catalysts, the chloride ions were easily removed because they were present near the surface of the catalyst. For the sol-gel catalyst washed by KOH aq. in more severe conditions, the conversion rate increased, from 42.0 to 59.8%. For the sol-gel catalysts, the chloride ions existed in the hard matrices of the support, which had been formed by the activation treatment at 673 K, and they were more difficult to remove. However, when the sol-gel catalyst was treated at relatively low temperature (473 K) in a hydrogen atmosphere, before washing with KOH aq., the catalyst had a high conversion rate (75.6%). This was comparable to that of the impregnation catalyst that was washed with distilled water. It appeared that the chloride ions could be removed from the catalyst by treatment at low temperature (473 K), owing to the imperfect fixing of the catalyst structure, namely the soft matrices, and a large positive effect was observed on removal of these chloride ions from both the sol-gel and impregnation catalysts. However, the high conversion rates obtained for the catalyst prepared from a chloride-free metal source were not observed for the sol-gel and impregnation catalysts with removed chloride ions.

TABLE 2
Effect of Catalyst Raw Materials on the Hydrogenation of Ethyl Phenylacetate[a]

Metal source		Method	Conversion	Selectivity
Ru	Sn	of preparation	(%)	(%)
$RuCl_3 \bullet nH_2O$	$SnCl_2 \bullet 2H_2O$	Sol-gel	37.8	98.5
$RuCl_3 \bullet nH_2O$	$SnCl_2 \bullet 2H_2O$	Impregnation	41.4	97.7
$Ru(acac)_3$	$Sn(OBu^n)_4$	Sol-gel	88.4	93.3
$Ru(acac)_3$	$Sn(OBu^n)_4$	Impregnation	91.9	94.9

[a]Experimental conditions were as follows: The impregnation of the support with ruthenium and tin was carried out in a conventional manner with ethanol as the solvent. The ruthenium metal loading was 5 wt%, and the atomic ratio of Ru/Sn was 1:2. Activation and reaction conditions for the catalysts were the same as those in Table 1.

TABLE 3
Effect of Washing on Catalyst Performance in Hydrogenation of Ethyl Phenylacetate[a]

Washing method	Preactivation temperature (K)	Conversion (%)	Selectivity (%)
Sol-gel catalyst			
No wash		37.8	98.5
H_2O	673	42.0	98.0
0.1 mol cm^{-3} KOH aq.	673	59.8	97.2
0.1 mol cm^{-3} KOH aq.	473	75.6	97.2
Impregnation catalyst			
No wash		41.4	97.7
H_2O	673	72.7	95.7
0.1 mol dm^{-3} KOH aq.	673	71.8	97.4

[a]The catalysts were prepared from $RuCl_3 \bullet nH_2O$ and $SnCl_2 \bullet 2H_2O$, and preactivated in a hydrogen stream for 4 h before washing. The catalysts were activated in a hydrogen stream at 673 K for 4 h before use. Other experimental conditions were the same as those in Table 2.

Effect of chloride-free tin source. Table 4 shows the effect of the tin source on the hydrogenation of ethyl phenylacetate. All tin source materials were chloride-free and soluble in some alcohol solvent. For tin(II) 2-ethylhexanoate, $[Sn(C_8H_{15}O_2)_2]$, which is insoluble in easily removed sol-

TABLE 4
Effect of Tin Source on the Hydrogenation of Ethyl Phenylacetate[a]

Tin source	Conversion (%)	Selectivity (%)
Sol-gel catalyst		
$Sn(OBu^n)_4$	88.4	93.3
$Sn(C_8H_{15}O_2)_2$	92.2	95.6
$Sn(acac)_2$	93.6	95.9
Impregnation catalyst		
$Sn(OBu^n)_4$	91.9	94.9
$Sn(acac)_2$	97.4	95.4

[a]Experimental conditions were the same as those in Table 2.

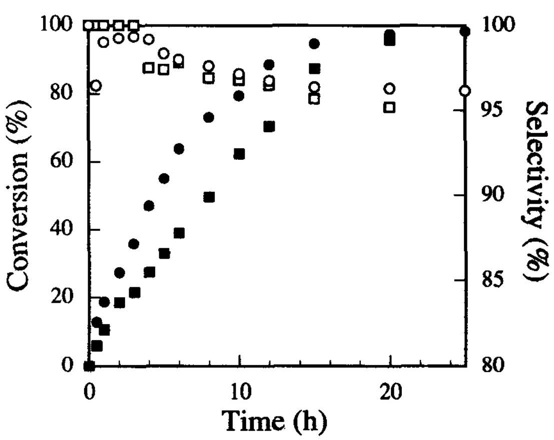

FIG. 2. Effect of the different catalyst preparation methods on the hydrogenation with time of ethyl phenylacetate with 5 wt% Ru/11.75 wt% Sn/Al_2O_3; ■: conversion, sol-gel, ●: conversion, impregnation, □: selectivity, sol-gel, ○: selectivity, impregnation.

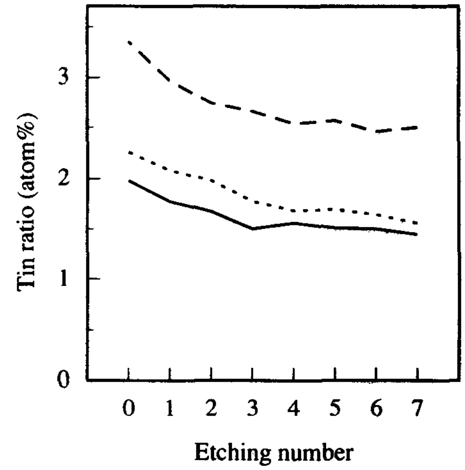

FIG. 4. Variation of the tin ratio with depth determined by X-ray photoelectron spectra; ——: sol-gel, — —: impregnation (impregnation order: Ru → Sn), – –: impregnation (impregnation order: Sn → Ru).

vents, e.g., ethanol, 2-methyl-2,4-pentanediol was used for the sol-gel catalyst preparation. All catalysts of both sol-gel and impregnation types were high, suggesting that selective hydrogenation of ethyl phenylacetate to 2-phenylethanol requires a chloride-free tin source.

Effect of catalyst preparation method. Figure 2 shows the effect of the different catalyst preparation methods on hydrogenation with time of ethyl phenylacetate. With regard to selectivity of 2-phenylethanol, the performances were comparable. However, in terms of the conversion rate, the impregnation catalyst was higher than the sol-gel catalyst. Figure 3 shows the effect of the metal-impregnation order on the hydrogenation with time of ethyl phenylacetate. The reaction results were comparable. It is often observed that the hydrogenation reaction of unsaturated C–C bonds is retarded by the addition of tin into noble-metal catalysts (11,12). However, tin in the catalysts shows a dramatic effect on the conversion of COOH and/or COOR groups to the corresponding alcohol groups during hydrogenation (5,6,13). Narasimhan *et al.* (13) have stated that hydrogenation of COOR groups with binary metal catalysts containing tin proceeds after the COOR groups were adsorbed on the tin and activated, accompanying the transfer of hydrogen dissociated on the noble metal to the COOR adsorbed. This clearly indicates that tin is one of the important active sites for the hydrogenation of COOR groups, and beside the selectivity, tin plays an important role for the catalyst activity as well as the noble metal. Figure 4 shows variation of the tin ratio, with depth, for each of the catalysts, as determined by XPS. These measurement indicated that the surface on the impregnation catalysts had a higher content of tin than that of the sol-gel catalysts. It is known that the components are homogeneously dispersed in solid catalysts prepared by the sol-gel method (14–16), and it is also assumed that the metals impregnated onto supports exist near the surface of the sold catalysts. These concepts are consistent with the results in Figure 4. Accordingly, it is reasonable that both impregnation catalysts showed higher conversion rates than sol-gel catalysts.

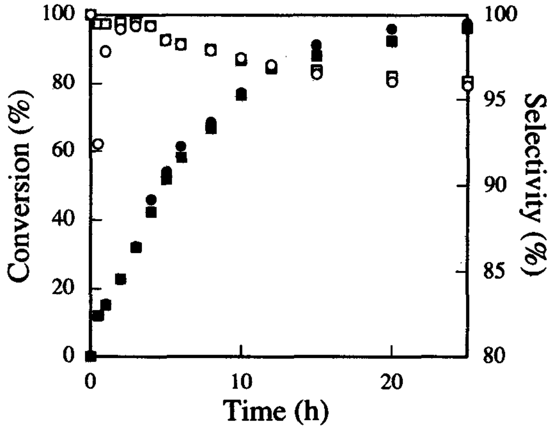

FIG. 3. Effect of metal-impregnation order on hydrogenation with time of ethyl phenylacetate; ■: conversion, impregnation order: Ru → Sn, ●: conversion, impregnation order: Sn → Ru, □: selectivity, impregnation order: Ru → Sn, ○: selectivity, impregnation order: Sn → Ru.

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