A new catalyst preparation by a combination of complexing agent-assisted sol–gel and impregnation methods

Kazuaki Ishii [a], Fujio Mizukami [b,*], Shu-ichi Niwa [b], Ryujiro Kutsuzawa [b], Makoto Toba [b] and Yuki Fujii [a]

[a] *Graduate School of Science and Engineering, Ibaraki University, Mito, Ibaraki 310, Japan*
[b] *National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan*

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The properties and preparation of a ruthenium–tin–alumina catalyst and its control by a combination of a complexing agent-assisted sol–gel method and an impregnation method have been investigated. It was found that the metal composition of the catalyst surface could be altered by use of the combination of the two preparation methods. Depending on the surface metal composition, the H_2-adsorption ability and the hydrogenation activity of the catalysts could also be changed.

Keywords: catalyst preparation method, ruthenium–tin–alumina, combination, sol–gel, impregnation, selective hydrogenation, benzoic acid, benzyl alcohol

1. Introduction

It is well known that the catalyst surface has great influence on catalytic activities and selectivities [1]. Therefore, controlling of the catalyst surface is very important in realizing functional group selective reactions.

We have already reported that ruthenium–tin–alumina ($Ru/Sn/Al_2O_3$) catalysts prepared by an improved sol–gel method hydrogenate selectively unsaturated carboxylic acids such as oleic acid to the corresponding unsaturated alcohols [2]. On the other hand, we found that a $Ru/Sn/Al_2O_3$ catalyst prepared by impregnation gives a higher yield for the formation of 2-phenylethanol in the hydrogenation of ethyl phenylacetate than the corresponding sol–gel catalyst [3]. These results suggest that the preparation method of the catalyst affects the surface properties to a greater extent; at the same time, the preparation method to be used should be changed, depending on the substrate.

As the first step to design a catalyst surface suitable for a selected substrate, it is here examined, using $Ru/Sn/Al_2O_3$ as the example, how the surface state of catalysts is changed by the preparation method. In addition, it is reported how the surface composition and properties of catalysts can be controlled by a combination of sol–gel and impregnation methods, shown in figure 1.

2. Experimental procedure

2.1. Preparation of catalyst

All chemicals were guaranteed reagent grade, unless otherwise stated. The precursors for ruthenium, tin and alumina were tris(acetylacetonato)ruthenium(III), $[Ru(acac)_3]$,

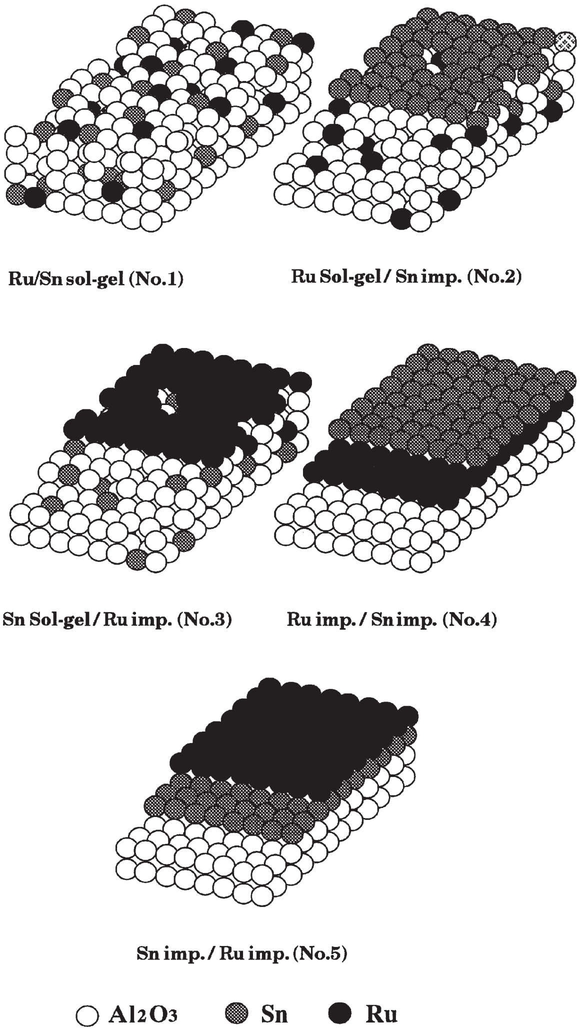
Ru/Sn sol-gel (No.1)
Ru Sol-gel / Sn imp. (No.2)
Sn Sol-gel / Ru imp. (No.3)
Ru imp. / Sn imp. (No.4)
Sn imp. / Ru imp. (No.5)

Figure 1. Postulated illustrations of the catalysts prepared by sol–gel, impregnation, and their combination.

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[*] To whom correspondence should be addressed.

tin n-butoxide, $[Sn(OBu^n)_4]$, and aluminum isopropoxide, $[Al(OPr^i)_3]$, respectively. The solvents used were 2-methyl-2,4-pentanediol in the sol–gel method, and ethanol in the impregnation method. $Ru(acac)_3$ was converted into the corresponding nitrate by treatment at ca. 353 K with nitric acid prior to catalyst preparation [2].

The preparation of ruthenium and tin solution is as follows: 24 g of concentrated nitric acid was carefully added to 1.18 g $Ru(acac)_3$, and then 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. 2.44 g $Sn(OBu^n)_4$ was dissolved in 20 cm^3 of ethanol.

Five types of 2 wt% Ru/4.7 wt% Sn/Al_2O_3 catalysts were prepared by different methods:

(i) Catalyst no. 1 (Ru/Sn sol–gel) – complexing agent-assisted sol–gel method [2–7]: 56 g $Al(OPr^i)_3$ and 65 g 2-methyl-2,4-pentanediol were mixed at room temperature and then heated to 393 K while stirring. After having completely dissolved, the isopropanol, which had been produced by ligand-exchange reaction, was removed *in vacuo* at 353 K. The ruthenium solution, which had been prepared beforehand, and ethanoic solution of $Sn(OBu^n)_4$ were then added, and the mixture was then stirred for 2 h at 353 K. The ethanol and butanol were then removed, again *in vacuo*, at the same temperature. 45 g of water was then added to the solution and the resultant 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.

(ii) Catalyst no. 2 (Ru sol–gel/Sn imp.): The catalyst was prepared via a combination of sol–gel and impregnation methods. Ruthenium was incorporated into the alumina by the sol–gel method previously described. Then the dry powder was further degassed at 473 K for 2 h and cooled. The ethanoic solution containing $Sn(OBu^n)_4$ was then added to the dry ruthenium–alumina powder, which had previously been prepared by the sol–gel method, and the mixture was aged overnight at room temperature, followed by the drying and activation procedure described before.

(iii) Catalyst no. 3 (Sn sol–gel/Ru imp.): The procedure for this catalyst was the same as that described for the catalyst no. 2, except that the tin was incorporated into the alumina by the sol–gel method first, then the ruthenium was incorporated by use of the impregnation method.

(iv) Catalyst no. 4 (Ru imp./Sn imp.): The alumina was prepared by the sol–gel method [8,9] described previously. The ruthenium solution was then impregnated onto the sol–gel alumina. After solvent removal and drying, the tin solution was impregnated onto the dry powder, impregnated with ruthenium, followed by drying and activation, as described previously.

(v) Catalyst no. 5 (Sn imp./Ru imp.): The procedure followed to produce this catalyst was the same as that for catalyst no. 4, except for the reversed sequence of impregnation of the ruthenium and tin.

(vi) Catalyst no. 6 (Ru sol–gel) – incorporating of ruthenium in alumina by the sol–gel method: The catalyst was prepared in a similar manner to that described above, except a tin compound was not used.

(vii) Catalyst no. 7 (Sn sol–gel) – incorporating of tin in alumina by the sol–gel method: The catalyst was prepared in a similar manner to that described above, except a ruthenium compound was not used.

2.2. Measurements

X-ray powder diffraction. The X-ray powder diffraction patterns were obtained on a Mac Science MXP-18 instrument using Cu K_α radiation with a Ni filter.

H_2 chemisorption. H_2 chemisorption on the catalysts was carried out at 523 K after evacuating the system at 673 K to 10^{-4} Pa for 3 h using a BELSORP 36 (Nihon Bell Co., Ltd.).

Specific surface area. Specific surface area was determined by the BET method from nitrogen-adsorption data at 77 K using a BELSORP 36 (Nihon Bell Co., Ltd.).

X-ray photoelectron spectroscopy. XPS were acquired on a Shimadzu (Tokyo, Japan) ESCA-1000 spectrophotometer with a 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. Quantification of the XPS spectra was carried out by taking the area ratios of the peaks. The areas were estimated by resolving the curves, assuming Gaussian peak shapes. The sputtering etching of the surface of the catalysts was carried out by Ar^+ (2 kV, 20 mA) bombardment.

Analysis of catalysts using X-ray fluorescence spectroscopy. The metal contents of the catalysts were measured using a Seiko-denshi (Tokyo, Japan) SEA 2010 X-ray fluorescence spectrometer.

Hydrogenation reaction. The hydrogenation reaction was undertaken in a 500 cm^3 reactor equipped with a pressure regulator. The reactor was charged with 20 g of benzoic acid and 180 g ethylene glycol monomethyl ether, together with 2 g of the catalyst, which was activated in an atmosphere of hydrogen at 673 K for 4 h 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 523 K and pressurized with hydrogen to 8.0 MPa. The speed of the stirrer to mix the solution was maintained at 1200 rpm. Samples were drawn during the course of the reaction for analysis. After 10 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 60 m × 0.25 mm capillary

Table 1
Properties of catalysts activated in hydrogen at 673 K for 4 h.

Preparation method (2 wt% Ru/4.7 wt% Sn/Al_2O_3)	Metal composition[a] Ru	Sn	Metal ratio Sn/Ru	H_2 chemisorption ml(STP)/g	ml(STP)/m^2	Surface area (m^2/g)
Ru/Sn sol–gel (no. 1)	0.013	0.028	2.33	9.1	2.3×10^{-2}	392
Ru sol–gel/Sn imp. (no. 2)	0.014	0.029	2.37	3.7	0.9×10^{-2}	454
Sn sol–gel/Ru imp. (no. 3)	0.016	0.036	2.44	10.5	2.7×10^{-2}	396
Ru imp./Sn imp. (no. 4)	0.018	0.040	2.36	11.6	3.4×10^{-2}	341
Sn imp./Ru imp. (no. 5)	0.017	0.041	2.41	11.8	3.8×10^{-2}	307
Ru sol–gel (no. 6)	–	–	–	7.9	1.6×10^{-2}	500
Sn sol–gel (no. 7)	–	–	–	0.8	0.8×10^{-2}	390
Al_2O_3	–	–	–	–	–	420

[a] Based on alumina.

column TC-1 (GL Science Co., Ltd., Japan) operated with temperature programming from 353 to 523 K at 5 K/min and with helium as the carrier gas. A flame-ionization detector was used. The acids and alcohols in the reaction mixtures were first converted to their silylic-derivative (by N,O-bis(trimethylsilyl)acetamide), respectively, without prior separation. Prior to silylation, the product mixture was first treated with anhydrous magnesium sulfate.

3. Results and discussion

3.1. Crystal structure, specific surface area and H_2 chemisorption

For the X-ray diffraction patterns of the catalysts after activation, it was difficult to observe a crystalline phase of the ruthenium and tin, except the diffraction corresponding to the γ-alumina phase, suggesting that the ruthenium and tin were well dispersed on the support, respectively.

Table 1 shows the specific surface areas determined by the BET methods from nitrogen-adsorption data and H_2-chemisorption data of the catalysts. For all catalysts, mesopores ranging from 7 to 9 nm were observed, suggesting that all catalysts have a similar pore distribution. The specific surface area of catalysts nos. 1–3, prepared by the sol–gel method, was larger than that of catalysts nos. 4 and 5, which were prepared by the impregnation method. It appears that the surface area of catalysts nos. 4 and 5 was covered with the metal elements and their oxides as a result of the impregnation.

For the H_2 chemisorption on catalysts no. 6 (ruthenium only) and no. 7 (tin only), the adsorbed amount of hydrogen on catalyst no. 7 was smaller than that of catalyst no. 6, suggesting the tin had a lower affinity for hydrogen compared with ruthenium. H_2 chemisorptions of the catalysts nos. 4 and 5, which were prepared by the impregnation method only, were larger than those of the other three, and the value of catalyst no. 5 was slightly larger than that of no. 4. With regard to the catalysts nos. 2 and 3, no. 3 adsorbed a greater amount of hydrogen than catalyst no. 2. It was also noted that H_2 chemisorption of the catalysts, which were impregnated with ruthenium second, was greater than for those catalysts, which were impregnated with tin second, and the difference in H_2 chemisorption between catalysts nos. 2 and 3 showed pronouncedly compared with catalysts nos. 4 and 5.

3.2. Bulk metal composition of the catalysts

Table 1 also shows the results of the analysis of the bulk metal composition of each of the catalysts, using X-ray fluorescence spectroscopy. The contents of the ruthenium and the tin were generally lower than the theoretical values. For the ratio of tin to ruthenium (Sn/Ru), the ratio was slightly higher than expected, however, all catalysts had a similar ratio of tin to ruthenium, suggesting that all catalysts have a nearly identical composition.

3.3. Metal composition of the catalyst near the surface

The metal contents of each catalyst from the surface to etching layer 11 are given in table 2. These results indicate that catalysts nos. 4 and 5 had higher metal contents in each layer, therefore, it appeared that the metal, which had been impregnated, existed near the surface.

Figure 2 shows the variation of the atomic ratio of tin to ruthenium, to a depth of 50 nm, based on silica, for each catalyst, as determined by XPS. For the catalysts prepared by a combined sol–gel and impregnation method, it was noted that the catalysts had a higher metal ratio of the element impregnated second, owing to impregnation after the first metal had been dispersed into the catalyst by the sol–gel method. For catalysts nos. 4 and 5, no effect related to the impregnation order was observed (see figure 2), suggesting that the ruthenium and the tin elements were mixed and dispersed during the second impregnation, owing the element first impregnated onto the support being unfixed, compared with that of the sol–gel method.

Regarding the atomic ratio of tin to ruthenium at the surface, all catalysts had a higher tin ratio than predicted. Catalysts nos. 4 and 5 had 3–4 times the estimated tin ratio, and catalysts nos. 2 and 3 twice. This indicated that the tin was diffused at the surface during activation in the H_2 atmosphere, or migrated and appeared to the surface during activation. However, with regard to the atomic ratio for catalyst no. 1, the tin ratio was slightly lower, because

Table 2
Metal content of catalysts from surface to layer 11 (50 nm).

Preparation method (2 wt% Ru/4.7 wt% Sn/Al_2O_3)	Metal content (calculation as metal) surface	 layer 1	 layer 6	 layer 11
Ru/Sn sol–gel (no. 1)	4.3	17.4	17.8	17.8
Ru sol–gel/Sn imp. (no. 2)	4.3	17.2	18.3	17.5
Sn sol–gel/Ru imp. (no. 3)	7.1	17.5	18.7	18.7
Ru imp./Sn imp. (no. 4)	10.2	21.1	22.6	22.8
Sn imp./Ru imp. (no. 5)	8.4	20.2	22.3	22.1

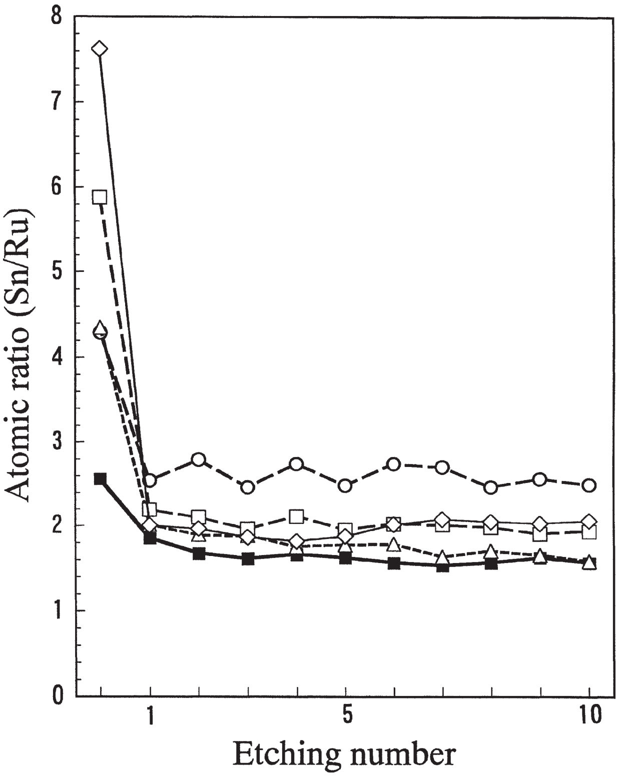

Figure 2. Variation of the metal ratio with depth of the catalyst activated in hydrogen at 673 K for 4 h, determined by XPS. (—■—) Catalyst no. 1 (Ru/Sn sol–gel); (–○– –) catalyst no. 2 (Ru sol–gel/Sn imp.); (– –△– –) catalyst no. 3 (Sn sol–gel/Ru imp.); (—◇—) catalyst no. 4 (Ru imp./Sn imp.); (–□– –) catalyst no. 5 (Sn imp./Ru imp.).

each metal element had been fixed onto the support by the sol–gel method.

Thus, the control of the surface layer using the impregnation method alone was difficult, however, the combination of sol–gel and impregnation methods was a convenient procedure for the control of the surface of the catalysts.

3.4. Hydrogenation of benzoic acid

Table 3 shows the effect of the different catalyst preparation methods on hydrogenation with time for benzoic acid. Although the results of the catalysts nos. 6 and 7 were not shown, catalyst no. 6 had a high conversion rate (100%) for 2 h, but poor selectivity (0%) for benzyl alcohol; mostly saturated products were obtained. On the other hand, catalyst no. 7 had a low conversion rate (about several percent) for 10 h, however, the selectivity of benzyl alcohol was almost 100%. It appeared the ruthenium contributed for the conversion rate, and the tin had a large influence on the selectivity for the formation of benzyl alcohol. For the comparison of the H_2-adsorption data (table 1) and the results of the hydrogenation reaction (table 3), it seemed that the catalysts, which had a larger adsorption amount of hydrogen, demonstrated high conversion rate.

For the combination catalysts nos. 2 and 3, catalyst no. 2 demonstrated a lower conversion rate, but a higher selectivity to benzyl alcohol compared with those of catalyst no. 3, suggesting that the effect of the impregnated element on the catalyst was stronger than that of the element incorporated by the sol–gel method. With regard to the impregnation catalysts nos. 4 and 5, on the other hand, the relationship of the conversion rate and selectivity between these catalysts showed a similar tendency to those of the combination catalysts, however, the difference of these were larger than for the combination catalysts.

For the selectivity of catalysts nos. 2 and 4, catalyst no. 4 demonstrated lower selectivity. Equally, the difference of the selectivity for catalysts nos. 3 and 5 was also found, and catalyst no. 3 showed a higher selectivity compared with catalyst no. 5. In this way, catalysts nos. 4 and 5 did not display such a higher selectivity, in spite of having a high tin content at the surface, however, it appeared that the total metal content on the surface of catalysts nos. 4 and 5 was greater than for the other catalysts (that is, the ruthenium content on the surface is also higher).

4. Conclusions

The components of the catalysts prepared by the sol–gel method are homogeneously dispersed, and the proportion of the metal elements reflected the ratio of Sn/Ru. For the catalysts prepared by the impregnation method, it was considered each layer of ruthenium and tin, which had been

Table 3
Effect of the different catalyst preparation methods on the hydrogenation with time of benzoic acid.

Catalyst	Benzoic acid conversion (%)		Benzyl alcohol selectivity (%)	
	8 h	10 h	8 h	10 h
Ru/Sn sol–gel (no. 1)	86.8	94.6	95.4	93.3
Ru sol–gel/Sn imp. (no. 2)	75.3	89.9	95.6	93.4
Sn sol–gel/Ru imp. (no. 3)	86.5	95.5	94.9	91.3
Ru imp./Sn imp. (no. 4)	91.1	97.3	94.3	91.7
Sn imp./Ru imp. (no. 5)	98.1	99.8	88.9	84.7

impregnated in a fixed order, were not formed at the surface, but the mixed components of the ruthenium and tin were dispersed on the surface. On the other hand, for the catalysts prepared by a combined method, the proportion of the metal element, which was impregnated second, was higher, and the impregnated element had a larger effect than the one incorporated by the sol–gel method. These results suggest that a combination of sol–gel and impregnation methods is a suitable and convenient procedure for the design and control of the surface component and reactivity of catalysts.

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