Unprecedented Reductive Esterification of Carboxylic Acids under Hydrogen by Reusable Heterogeneous Platinum Catalysts

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Abstract: Supported metal catalysts have been tested for an unprecedented reductive dimerization of carboxylic acids to esters under 8 bar hydrogen in solvent-free conditions. Among various metal-loaded tin oxide catalysts, platinum-loaded tin dioxide (Pt/SnO_2) shows the highest ester yield for the reaction of dodecanoic acid. Among Pt catalysts on various supports, Lewis acidic oxides, especially SnO_2, show high activity. The most active catalyst, 5 wt% Pt/SnO_2 reduced at 100°C, is effective for the reductive esterification of various carboxylic acids, and the catalyst is reusable for nine cycles, demonstrating the first successful example for the title reaction. Infrared (IR) studies of a model compound (formic acid) on some metal oxides indicate a strong Lewis acid-base interaction between SnO_2 and the carbonyl oxygen. For Pt/SnO_2 catalysts with different Pt particle sizes, the activity increases with decreasing size of Pt metal. A cooperative catalysis of the Pt metal nanoparticles and the Sn^{4+} Lewis acid sites is proposed.

Keywords: carboxylic acids; esters; heterogeneous catalysis; hydrogenation; platinum; tin

Introduction

The synthesis of esters plays a major role in organic synthesis in academic research and industrial production of chemicals.[1] Conventionally, esters are produced by condensation of a carboxylic acid or activated acid derivatives (acid chlorides or anhydrides) with excess amounts of an alcohol in the presence of an acid catalyst or a dehydrating agent, producing large amount of wastes. Environmentally benign synthetic methods such as condensation of an equimolar amount of carboxylic acid and alcohol,[2] esterification of aldehydes with alcohols,[3] dimerization of two aldehydes (Tishchenko reaction)[4] and dehydrogenative dimerization of two primary alcohols[5,6] were reported. In response to the increasing demand for simple and environmentally benign procedures, development of a novel direct route to esters from stable and readily available substrates still remains a major challenge. Potentially, esters can be synthesized by reduction of carboxylic acids as stable and readily available starting materials. Sakai et al. reported the first example of reductive esterification of carboxylic acids with 3 equiv. of Et$_3$SiH catalyzed by InBr$_3$ with 0.1 equiv. of H$_2$SO$_4$.[7] However, this system suffers from drawbacks such as need for expensive reductant (Et$_3$SiH) and acidic conditions, high catalyst loading (5 mol%) and difficulties in catalyst/product separation and catalyst reuse. Reductive esterification of carboxylic acids by H$_2$ as an ideal method is difficult, because carboxylic acids are among the most difficult carbonyl substrates to hydrogenate due to the low electrophilicity of the carbonyl carbon.[8] Goldberg et al. reported the selective hydrogenation of glacial acetic acid to ethyl acetate under 27 bar H$_2$ by homogeneous Ir or Rh catalysts,[9a] but the yields of ethyl acetate were low, and the system was limited to acetic acid. Previous reports on the formation of esters by hydrogenation of carboxylic acid by homogenous Ru catalysts suffer from low conversion and low selectivity to the esters.[9b,c] Hydrogenation of carboxylic acids by heterogeneous catalysts generally gives alcohols[10] or alkanes.[11a] In the course of our studies on support-controlled selective reductive transformations of carboxylic acids by heterogeneous Pt catalysts,[11] we have discovered the first successful example of the reductive esterification of various carboxylic acids by H$_2$ (8 bar) under additive-free and solvent-free conditions by SnO_2-supported Pt (Pt/SnO_2) as a reusable heterogeneous catalyst. We report herein the catalytic

properties of this new catalytic system. We also study the structure-activity relationship to address the influences of the electronic structure of the supported metals, Lewis acidic nature of the support oxides, size and phase of Pt on the activity.

Results and Discussion

Optimization of Catalysts and Conditions

As summarized in Table 1, we screened 18 types of the supported transition metal catalysts, pre-reduced in H_2 at 100 °C for 0.5 h, for hydrogenation of dodecanoic acid in solvent-free conditions under 8 bar H_2 at 200 °C for 24 h. First, we tested various transition metal (Pt, Rh, Ru, Pd, Ir, Re, Ni, Cu, Co, Ag) catalysts supported on SnO_2 (entries 1–10). Among the catalysts tested, Pt/SnO_2 showed the highest yield (90%) of the corresponding ester, dodecyl dodecanoate. 1-Dodecanol was observed as a by-product in 3% yield. Rh/SnO_2 also showed high yield (85%), and Ru- and Re-loaded SnO_2 showed moderate yields (50–54%). Entries 12–18 show the results of Pt catalysts loaded on other supports (ZrO_2, TiO_2, Al_2O_3,

Table 1. Catalyst screening for reductive esterification of dodecanoic acid.

$$R\overset{O}{\underset{}{\overset{\|}{C}}}OH + H_2 \xrightarrow[\substack{\text{solvent-free} \\ 200\,°C,\ 24\,h}]{\text{cat. (1 mol\%)}} 1/2\ R\overset{O}{\underset{}{\overset{\|}{C}}}O\overset{}{\diagdown}R + H_2O$$

R = n-C₁₁H₂₃   8 bar
1 mmol

Entry	Catalyst	Conv. [%]	Yield [%][a]
1	Pt/SnO₂	95	90 (3)[b]
2	Rh/SnO₂	90	85 (2)[b]
3	Ru/SnO₂	61	54
4	Re/SnO₂	53	50
5	Pd/SnO₂	58	38
6	Ir/SnO₂	37	30
7	Ni/SnO₂	3	3
8	Cu/SnO₂	1	1
9	Co/SnO₂	0	0
10	Ag/SnO₂	0	0
11	SnO₂[c]	0	0
12	Pt/ZrO₂	71	63
13	Pt/TiO₂	59	45 (2)[d]
14	Pt/Al₂O₃	56	17
15	Pt/CeO₂	52	12 (1)[d]
16	Pt/HZSM5	11	3 (2)[d]
17	Pt/SiO₂	7	1
18	Pt/C	0	0
19	blank	0	0

[a] GC yields.
[b] Yield of 1-dodecanol.
[c] Catalyst amount was 39 mg.
[d] Yield of n-dodecane.

**Table 2.** Reductive esterification of dodecanoic acid.[a]

Entry	Solvent	Conv. [%]	Yield [%][b]
1	no solvent	95	90 (3)
2	o-xylene	93	88 (2)
3	diglyme	91	84 (4)
4	mesitylene	94	83 (3)
5	n-octane	92	79 (3)
6	H₂O	41	27 (9)

[a] 1 mol% Pt/SnO₂, 1 mmol dodecanoic acid, 0 or 1 g solvent, 200 °C, 24 h.
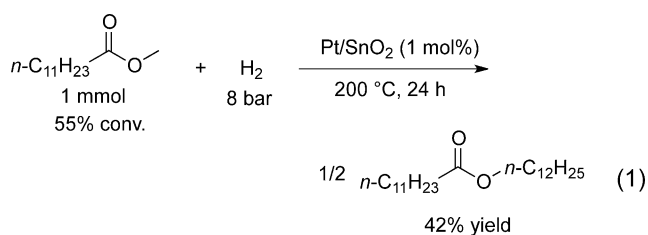[b] GC yields. Yields of 1-dodecanol are in the parentheses.

CeO₂, HZSM5 zeolite, SiO₂, C). Pt/SnO_2 (entry 1) showed a higher yield of the ester (91%) than the other Pt-loaded catalysts. Pt/ZrO_2 and Pt/TiO_2 (entries 12 and 13) gave moderate yields (45–63%), and the Pt loaded on Al_2O_3, CeO_2, HZSM5 zeolite and SiO_2 (entries 14–17) showed low yields (1–17%). A commercially available carbon-supported Pt as a conventional Pt catalyst was inactive (entry 18). From these results, Pt/SnO_2 is found to be the most effective catalyst among the catalysts tested in Table 1. Taking into account that SnO_2 (entry 11) and Pt nanoparticles loaded on an inert support (Pt/C) are inactive for the hydrogenation of dodecanoic acid to the ester, it is suggested that the high activity of Pt/SnO_2 is due to a synergistic effect of SnO_2 and Pt. It should be noted that Pt/SnO_2 is also effective for the acceptor-less dehydrogenative dimerization of two primary alcohols to esters as reported in our previous study.[5a]

Next, we optimized the reaction conditions for the hydrogenation of dodecanoic acid to the ester by 1 mol% of Pt/SnO_2. Table 2 shows the effect of solvent on the yield of the ester and 1-dodecanol as a by-product for the reaction under 8 bar H_2 at 200 °C. The reaction under the solvent-free conditions gave the highest yield of the ester (90%). Reactions in various organic solvent (entries 2–5) were also successful, which gave 79–88% yield of the ester. The reaction in water gave the lowest yield (27%). Under the solvent-free conditions, the reaction at a lower temperature (180 °C) resulted in lower yield (84%) than that at 200 °C (91%). The reaction under lower H_2 pressure (5 bar) at 200 °C resulted in lower yield (80%) than that under standard H_2 pressure (8 bar). A decrease in the catalyst amount from 1 mol% to 0.5 mol% decreased the ester yield from 90% to 59%. The time course of the reaction under the standard conditions (Figure 1) shows that the reaction time of 24 h is enough to obtain a high yield of the ester. Further reduction of the ester to ether was not observed. An interesting feature in Figure 1 is the fact that the carboxylic acid is more reactive than the ester (dodecyl dodecanoate), because normally esters are more reactive than carboxylic acids in hydrogenation reac-
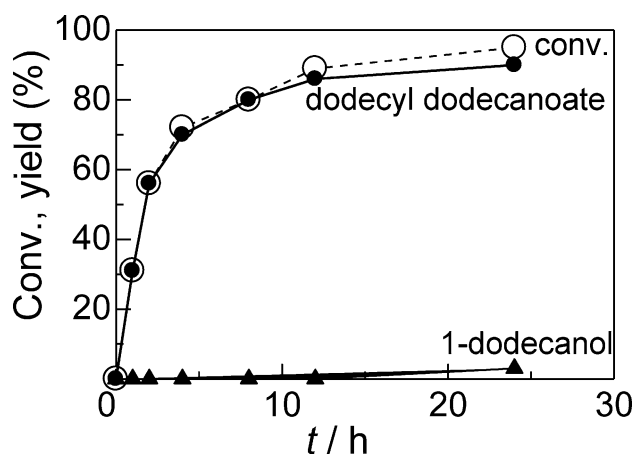
Figure 1. Time-yield profile under the conditions in Table 1.

Figure 2. Reuse of Pt/SnO$_2$ for reductive esterification of dodecanoic acid under the conditions in Table 1.

tions by organometallic catalysts.[8] This unusual trend could be partly due to steric hindrance of the large ester, which was supported by the finding that the hydrogenation of a smaller ester (methyl dodecanoate) resulted in a moderate yield of dodecyl dodecanoate as shown in the Eq. (1). However, the lower yield (42%) in Eq. (1) than that in the standard hydrogena-

$$n\text{-}C_{11}H_{23}\!\!-\!\!C(=O)\!\!-\!\!O\!\!-\!\!CH_3 \;+\; H_2 \;\xrightarrow[\text{200 °C, 24 h}]{\text{Pt/SnO}_2\,(1\,\text{mol\%})}\; \tfrac{1}{2}\; n\text{-}C_{11}H_{23}\!\!-\!\!C(=O)\!\!-\!\!O\!\!-\!\!n\text{-}C_{12}H_{25} \quad (1)$$
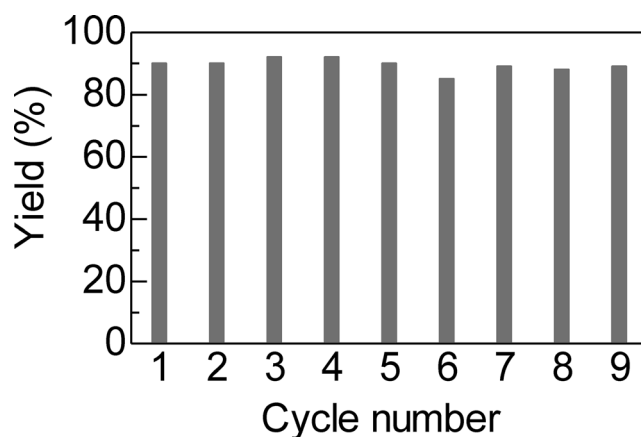
1 mmol   8 bar
55% conv.

42% yield

tion of dodecanoic acid (90%) suggests that carboxylic acids are intrinsically more reactive than esters in this heterogeneous catalytic system.

Another explanation might be that the carboxylic acid is converted first to its anhydride which then hydrogenates faster than the ester. However, the following results excluded this possibility; hydrogenation of stearic acid anhydride in the standard conditions did not give any hydrogenation products and SnO$_2$ did not show any activity for the anhydride formation from stearic acid at 200 °C.

Catalytic Properties of Pt/SnO$_2$

Under the optimized conditions with the most effective catalyst (Pt/SnO$_2$), we studied the catalytic properties of this catalytic system. As shown in Figure 2, Pt/SnO$_2$ was reusable for the reductive esterification of dodecanoic acid. After the first cycle, 2-propanol (6 mL) was added to the reaction mixture and catalyst
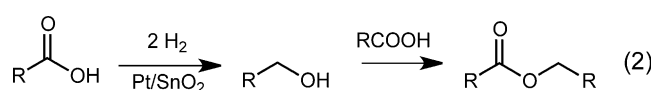
was separated by centrifugation. For each successive use, the recovered catalyst was washed by 2-propanol three times, followed by centrifugation and drying in an oven at 100 °C for 3 h, followed by H$_2$ reduction at 100 °C for 0.5 h. The recovered catalyst was reused eight times without a marked loss of its catalytic activity. After the first cycle, ICP-AES analysis of the solution confirmed that the content of Pt in the solution was below the detection limit (10 ppb) and that of Sn was quite low (8 ppm, 0.008% of Sn in the catalyst used). These results indicate that Pt/SnO$_2$ acts as a reusable heterogeneous catalyst for this reaction.

Table 3 shows the general applicability of the present catalytic system with 1 mol% of Pt/SnO$_2$. After the reactions, the catalyst was removed from the mixture and the esters were isolated by column chromatography, resulting in moderate to high isolated yields (52–93%) of the corresponding esters. Linear, branched and cyclic aliphatic carboxylic acids (entries 1–8) underwent selective reductive esterification, producing the esters in moderate to high isolated yields. Aliphatic carboxylic acids with aromatic functional groups (entries 9–11) and benzoic acid derivatives (entries 12 and 13) were also selectively converted to the corresponding esters, without undergoing hydrogenation of the aromatic nuclei.

Possible Pathway

We discuss a possible pathway of the reaction. Reductive self-esterification of two carboxylic acids by H$_2$ may occur *via* two possible pathways: (a) reduction of one carboxylic acid to an alcohol, followed by its reaction with another carboxylic acid to give an ester,

$$R\text{-}COOH \;\xrightarrow[\text{Pt/SnO}_2]{2\,H_2}\; R\text{-}CH_2OH \;\xrightarrow{R\text{COOH}}\; R\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}R \quad (2)$$

Table 3. Reductive esterification of various carboxylic acids by Pt/SnO$_2$.

$$R\text{-}COOH + H_2 \xrightarrow[200\,°C,\ 24\ h]{Pt/SnO_2\ (1\ mol\%)} 1/2\ R\text{-}CO\text{-}O\text{-}R + H_2O$$

1 mmol   8 bar

Entry	Product	Isolated yield [%]
1	C$_{17}$H$_{35}$-n ···O-n-C$_{18}$H$_{37}$	82
2	C$_{15}$H$_{31}$-n ···O-n-C$_{16}$H$_{33}$	55
3	C$_{13}$H$_{27}$-n ···O-n-C$_{14}$H$_{29}$	86
4	C$_{11}$H$_{23}$-n ···O-n-C$_{12}$H$_{25}$	87
5	C$_9$H$_{19}$-n ···O-n-C$_{10}$H$_{21}$	93
6	n-C$_5$H$_{11}$ ···O-n-C$_6$H$_{13}$	59
7		86
8		73
9		91
10		85
11		89
12		72
13		52

value is more than 4 times faster than the Pt/SnO$_2$-catalyzed reductive dimerization n-dodecanoic acid to the ester (0.3 mmol h^{-1}). This result is consistent with the absence of 1-dodecanol in the initial period of the time course (Figure 1), and thus supports the pathway (a) shown in the Eq. (2). Pt/SnO$_2$-catalyzed hydrogenation of one carboxylic acid to an alcohol is slow, and its thermal esterification with another carboxylic acid is fast.

Factors Affecting the Catalytic Activity

We studied the relationship between various structural parameters and catalytic activity for the hydrogenation of dodecanoic acid (in 8 bar H$_2$ at 200 °C) to discuss important factors affecting the catalytic activity in the present system. First, we discuss a possible reason why Pt/SnO$_2$ gives a higher yield of the ester than other transition metal-loaded SnO$_2$ catalysts (Table 1, entries 1–10). The yields of the ester are replotted in Figure 3 as a function of the d-band center (ε_d) relative to the Fermi energy (E_F), $\varepsilon_d - E_F$, for the clean metal surface computed by Hammer and Nørskov,[12a] which has been used as a descriptor of activity trends in various transition metal surfaces.[12,13] Clearly, the platinum group metal (Pt, Ir, Pd, Rh, Ru) catalysts having intermediate $\varepsilon_d - E_F$ values show higher catalytic activity than the metals with low $\varepsilon_d - E_F$ values (Ag and Cu) and those with high $\varepsilon_d - E_F$ values (Ni and Co). Taking into account the facts that the bond strength between a metal surface (M) and a hydrogen atom (H) is weaker for a metal with lower $\varepsilon_d - E_F$ value[12a] and that the catalytic hydrogenation includes the formation and dissociation of M−H bonds, the result in Figure 3 suggests that the moderate M−H bond strength is favorable for this catalyt-
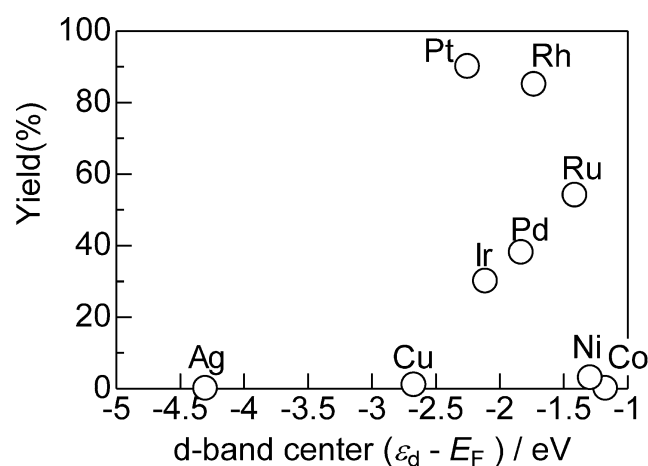
as shown in the Eq. (2), or (b) reduction of two carboxylic acids to aldehydes, followed by their disproportionation (Tishchenko reaction) to give the ester.

In our previous study, we showed that the reaction of 1 mmol of n-octanal in the presence of Pt/SnO$_2$ resulted in no formation of the corresponding ester, which ruled out the contribution of the route (b). Combined with the fact that 1-dodecanol is observed as a by-product in the reductive esterification of n-dodecanoic acid (Figure 1), the reaction can proceed via the route (a). The esterification of 1 mmol n-dodecanoic acid with 1 mmol 1-dodecanol under N$_2$ in the absence of the catalyst at 200 °C for 0.5 h gave the corresponding ester in 65% yield, corresponding to the thermal esterification rate of 1.3 mmol h^{-1}. This

Figure 3. Effect of the d-band center of metals relative to the Fermi energy (ε_d-E_F)[12a] on the yield of the ester (from Table 1) for the reductive esterification of dodecanoic acid by the SnO$_2$-supported transition metals.
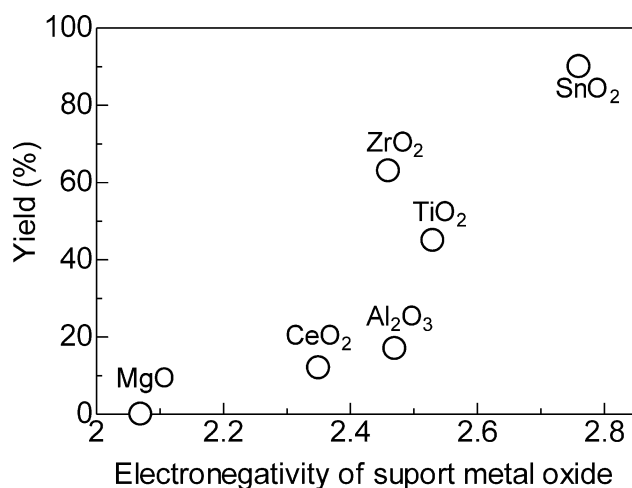
Figure 4. Effect of electronegativity of the metal oxide support on the yield of the ester (from Table 1) for the reductive esterification of dodecanoic acid by Pt-loaded metal oxides.

Figure 5. IR spectra of formic acid adsorbed on SnO_2, SiO_2 and TiO_2 at −70 °C.

ic system. The former metals (Ag and Cu) can show lower activity for the H_2 dissociation step than platinum-group-metals, while strong M−H bonds on the latter metals (Ni and Co) can result in slow rate of the H-transfer to the carboxyl group. Consequently, platinum group metal catalysts with moderate bond strength give high activity. This tendency has been observed for several catalytic systems.[12,13]

Next, we discuss a possible reason why SnO_2 was more effective than the other support materials. Table 1 shows that Pt/SnO_2 shows more than 90 times higher yield than the Pt catalysts on nearly neutral supports (Pt/C and Pt/SiO_2) and SnO_2 itself has no activity, which indicates that co-presence of Pt and SnO_2 support is necessary for this reaction. The ester yield for the Pt catalysts loaded on various metal oxides (from Table 1) is plotted in Figure 4 as a function of the electronegativity of the support metal oxide, which is generally used as a parameter of acidity of metal oxides.[14] There is a trend that the yield increases with increase in the electronegativity of the support. A basic support (MgO) is least active, acid-base bifunctional supports (CeO₂, Al₂O₃, ZrO₂, TiO₂) shows lower yields than an acidic support (SnO₂). SnO_2 is a well known promoter of platinum group metal catalysts for the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols; the addition of SnO_2 increase the selectivity of C=O bond reduction.[15] Nishiyama et al.[15] studied IR experiments of the adsorption of propionaldehyde on Rh/SnO_2 and showed that the C=O bond of the aldehyde ad-species was activated by the Lewis acid-base interaction between Sn cations and carbonyl oxygen. For hydrogenation of esters with SnO_x-promoted Ru catalysts, Ru was believed to activate H_2 and Sn species were believed to activate carbonyl groups.[16] To study
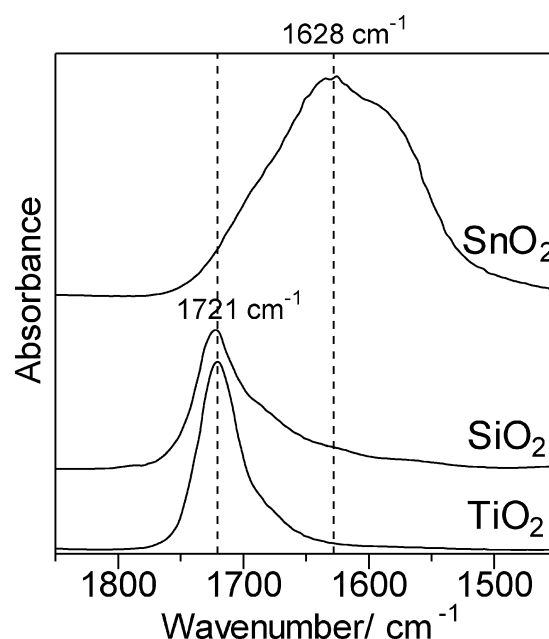
the Lewis acid-base interaction between the Sn cation and the carbonyl oxygen of a carboxylic acid, we carried out IR experiments on formic acid adsorbed on SnO_2, TiO_2 and SiO_2 at −70 °C (Figure 5). The formic acid adsorbed on SnO_2 showed the C=O stretching band at lower wavenumber (1628 cm⁻¹) than those on a non-Lewis acidic oxide, SiO_2 (1721 cm⁻¹). This indicates a strong Lewis acid-base interaction between the oxygen atom of the carboxyl group (Lewis base) and the Sn^{4+} cation (Lewis acid site). From the above results, we propose that SnO_2 acts as a Lewis acid to activate a carboxyl group. The electrophilic C=O group on Sn^{4+} can undergo nucleophilic attack of a hydride on the catalyst to give an alcohol, which then undergoes thermal esterification with another carboxylic acid.

Then, we studied the effect of the reduction temperature of Pt/SnO_2 on the initial rate of the ester formation measured under the conditions where conversion was below 30%. As shown in Figure 6, an increase in the reduction temperature from 100 °C to 400 °C decreased the reaction rate per total Pt atoms in the catalyst. The structure of the Pt species in the Pt/SnO_2 catalysts reduced at various temperatures was studied by X-ray diffraction (XRD) (Figure 7). The XRD pattern of the catalyst reduced at 100 °C showed broad and weak lines due to Pt metal together with the lines due to SnO_2. The XRD patterns of the Pt/SnO_2 catalysts reduced at high temperatures (300 and 400 °C) do not show lines due to Pt metal but lines due to intermetallic compounds of Pt and Sn (PtSn, Pt_3Sn and $PtSn_4$).[17] The number of catalytically available Pt(0) atoms on the surface of Pt-loaded
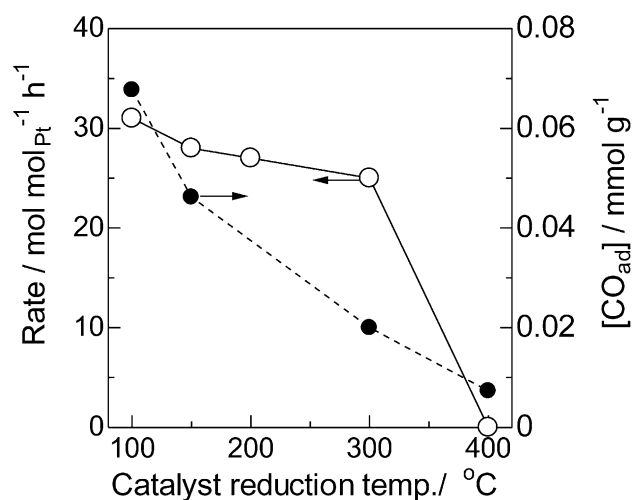
Figure 6. Effect of H_2 reduction temperature of Pt/SnO_2 catalysts (Pt = 5 wt%) on the initial rate per total Pt atom in the catalyst used for the reductive esterification of dodecanoic acid and the number of surface Pt(0) sites on the catalystsestimated by CO adsorption.
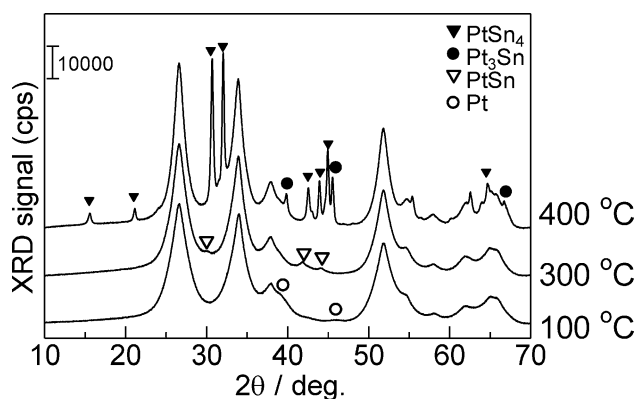
Figure 7. XRD patterns of 5 wt% Pt/SnO_2 reduced at 100, 300 and 400 °C.

catalysts is estimated by CO adsorption at room temperature. As shown in Figure 6, the number of CO adsorbed on the Pt/SnO_2 catalysts decreased with increasing reduction temperature. This trend is similar to the trend in the catalytic activity co-plotted in Figure 6. Combined with the XRD and XPS results, we can conclude that the decrease in the activity of the Pt/SnO_2 catalysts reduced at high temperatures (300 and 400 °C) is caused by the transformation of Pt metal to the intermetallic compounds (PtSn, Pt_3Sn and $PtSn_4$), whose surface has a lesser number of catalytically available Pt(0) atoms. Watson[18] et al. calculated the adsorption energies of hydrogen on Pt(111) and PtSn(111) surfaces and showed that doping with tin decreased the adsorption energy of hydrogen. van Bokhoven et al. studied the electronic structure of supported Pt and PtSn catalysts by Pt L_3 X-ray absorption spectroscopy and showed that the platinum d-band of PtSn particles was shifted down relative to
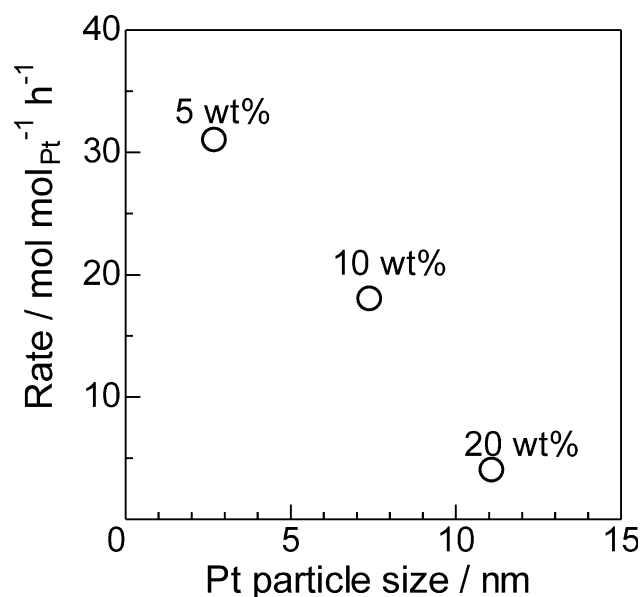
Figure 8. Initial rates per total Pt atom for the reductive esterification of dodecanoic acid by Pt/SnO_2 catalysts vs average size of Pt particle.

the Fermi level in comparison to Pt particles and thus, the incorporation of tin decreased the ability of hydrogen.[19] This can be the fundamental reason for the low catalytic activity of Pt/SnO_2 catalysts reduced at high temperatures (300 and 400 °C) in our catalytic system.

Finally, we studied the dependence of the catalytic activity on the size of Pt metal particles in Pt/SnO_2 reduced at low temperature (100 °C). A series of Pt/SnO_2 catalysts with different particle sizes were prepared by changing the Pt loading. As shown in the Supporting Information, Figure S1, the XRD patterns of the Pt/SnO_2 catalysts with high Pt loading (10 and 20 wt%) showed the lines due to Pt metal, and the average size of Pt metal crystallites was estimated from the broadening of the line at $2\theta = 46.4°$ using the Scherrer equation. As for the 5 wt% Pt/SnO_2 catalyst, the lines due to Pt metal were too weak, and thus we estimated the average size of Pt metal particles using the CO uptake assuming that CO was adsorbed on the surface of spherical Pt particles at a stoichiometry of CO/(surface Pt atom) = 1/1. As shown in Figure 8, the initial rate of the ester formation per total Pt atoms decreased with the mean diameter of Pt particles.

Summarizing the studies on the structure-activity relationship, we can conclude that small Pt metal nanoparticles supported on a Lewis acidic support, SnO_2, are active species for the reductive esterification of carboxylic acids. Combined with the possible reaction pathway in Eq. (2), we propose a cooperative catalysis of the Pt metal nanoparticles and the Sn^{4+} Lewis acid sites as follows. The Pt nanoparticles convert H_2 to the hydrogen atoms on the Pt surface (Pt–

H). The Lewis acid sites adjacent to the Pt sites increase the electrophilicity of the C=O group of the carboxylic acid adsorbed on the Sn^{4+} site, which undergoes nucleophilic attack of the Pt–H species to give an alcohol. The alcohol finally undergoes thermal esterification with another carboxylic acid.

Conclusions

We have reported an unprecedented reductive dimerization of two carboxylic acids to produce esters under H_2 in additive-free and solvent-free conditions using Pt metal nanoparticles-loaded SnO_2 as a reusable heterogeneous catalyst. The various aliphatic and aromatic carboxylic acids were selectively transformed to the corresponding esters, and the catalyst was reusable. Studies on the structure-activity relationship for various metal-loaded catalysts showed that the activity depended on the electronic states of the supported metals, Lewis acidic nature of the support materials and the phase and the size of metallic Pt species. A possible reason why Pt/SnO_2 gives higher activity than other transition metal-loaded SnO_2 catalysts is its moderate level of the d-band center (relative to the Fermi energy), which can result in a moderate activity for the H_2 dissociation and hydrogen-transfer steps. In supported Pt catalysts, the active catalyst must have three characteristics: (i) small size of Pt metal nanoparticles, (ii) no formation of Pt-Sn intermetallic compounds and (iii) a Lewis acidic support (SnO_2) which shows a strong acid-base interaction with the C=O group of carboxylic acids. We propose a cooperative catalysis of the Pt metal nanoparticles and the Sn^{4+} Lewis acid sites, in which the Pt site convert H_2 to the hydrogen atoms on the Pt site and the Lewis acid sites increase the electrophilicity of the C=O group of a carboxylic acid, which then undergoes nucleophilic attack of the hydrogen atoms on the Pt sites.

Experimental Section

General

Commercially available organic compounds (from Tokyo Chemical Industry or Kanto Chemical) were used without further purification. The GC (Shimadzu GC-2014) and GC-MS (Shimadzu GCMS-QP2010) analyses were carried out with an Ultra ALLOY capillary column UA+-1 (Frontier Laboratories Ltd.) using nitrogen and He as the carrier gas.

Preparation and Characterization of Catalysts

SnO_2 was prepared by calcination of H_2SnO_3 (Kojundo Chemical Laboratory Co., Ltd.) at 500°C for 3 h. ZrO_2 was prepared by calcination (500°C for 3 h) of $ZrO_2 \cdot n H_2O$ prepared by hydrolysis of zirconium oxynitrate dihydrate in

water by aqueous NH_4OH solution, followed by filtration of precipitate, washing with water three times, and drying at 100°C for 12 h. γ-Al_2O_3 was prepared by calcination of γ-AlOOH (Catapal B Alumina obtained from Sasol) for 3 h at 900°C. TiO_2 (JRC-TIO-4) and CeO_2 (JRC-CEO-3) were supplied from Catalysis Society of Japan. HZSM5 (SiO_2/Al_2O_3 = 22.3) was supplied from Tosoh Co. SiO_2 (Q-10, 300 $m^2 g^{-1}$) was supplied from Fuji Silysia Chemical Ltd.

The precursor of Pt/SnO_2 was prepared by an impregnation method. A mixture of SnO_2 and an aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ was evaporated at 50°C, followed by drying at 90°C for 12 h, and by calcination in air at 500°C for 3 h. Before each catalytic experiment, the Pt/SnO_2 catalyst (with Pt loading of 5 wt%) was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H_2 (20 $cm^3 min^{-1}$) at 100°C for 0.5 h. Other supported Pt catalysts (Pt = 5 wt%) were prepared by the same method. SnO_2-supported metal catalysts, M/SnO_2 (M = Ni, Cu, Co, Ag, Pd, Ru, Rh, Re, Ir), with metal loading of 5 wt% were prepared by the impregnation method in the similar manner as Pt/SnO_2 using aqueous solution of metal nitrates (for Ni, Cu, Co, Ag), $RuCl_3$, $IrCl_3 \cdot n H_2O$, NH_4ReO_4 or aqueous HNO_3 solution of $Pd(NO_3)_2$. A commercial Pt-loaded carbon catalyst (Pt/C, Pt = 5 wt%) was purchased from N.E. Chemcat, Corporation.

XRD patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. The numbers of surface metal atoms in Pt/SnO_2, pre-reduced in H_2 at 100, 300 and 400°C, were estimated from the CO uptake of the samples at room temperature using the pulse-adsorption of CO in a flow of He by BELCAT (BEL Japan).

Typical Procedures of Catalytic Reactions

Pt/SnO_2 (39 mg; 1 mol% Pt with respect to carboxylic acid) pre-reduced at 100°C was used as a standard catalyst. After the pre-reduction, the catalyst in the closed glass tube sealed with a septum inlet was cooled to room temperature under an H_2 atmosphere. n-Hexadecane (0.25 mmol) was injected onto the pre-reduced catalyst inside the glass tube through the septum inlet. Then, the septum was removed under air, and carboxylic acid (1 mmol) and a magnetic stirrer was put in the tube, followed by inserting the tube inside a stainless autoclave with a dead space of 30 cm^3. Soon after being sealed, the reactor was flushed with H_2 from a high pressure gas cylinder and charged with H_2 (typically 8 bar) at room temperature. Then, the reactor was heated at 200°C under stirring (500 rpm). Conversion and yields of products were determined by GC using n-hexadecane as an internal standard.

For the catalytic experiments in Table 3, we determined isolated yields of the esters as follows. After the reaction, 2-propanol (3 mL) was added to the reaction mixture and catalyst was separated by filtration. The products in the filtrate were concentrated by evaporation to remove volatile compounds. Then, the ester was isolated by column chromatography using silica gel 60 (spherical, 63–210 μm, Kanto Chemical Co. Ltd.) with hexane/ethyl acetate (5/95 to 10/90) as the eluting solvent, followed by analyses by ^{1}H NMR, ^{13}C NMR and GC-MS equipped with the same column as GC.

Acknowledgements

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