



Title	TiO ₂ -Supported Re as a General and Chemoselective Heterogeneous Catalyst for Hydrogenation of Carboxylic Acids to Alcohols
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TiO₂-Supported Re as a General and Chemoselective Heterogeneous Catalyst for Hydrogenation of Carboxylic Acids to Alcohols

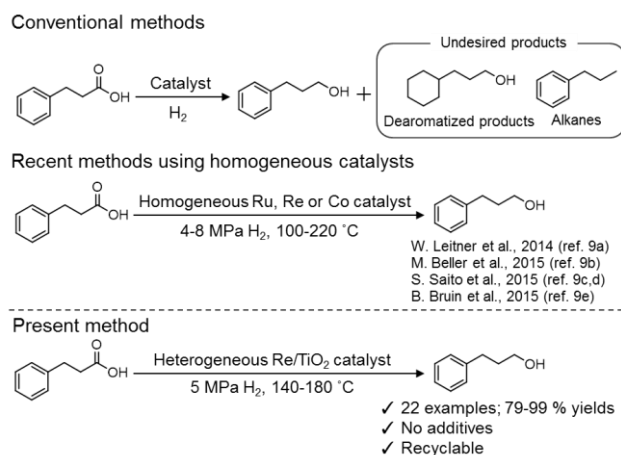
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Abstract: TiO₂-supported Re, Re/TiO₂, has been found to promote selective hydrogenation of aromatic and aliphatic carboxylic acids to alcohols. Re/TiO₂ is superior to other transition metal-loaded TiO₂ and supported Re catalysts for selective hydrogenation of 3-phenylpropionic acid. This process produces 3-phenylpropanol in a 97% yield under mild condition (5 MPa H₂ at 140 °C). Contrary to typical heterogeneous catalysts, Re/TiO₂ does not give dearomatized byproducts. The catalyst is recyclable and shows wide substrate scope toward the alcohol forming process (22 examples; up to 97% isolated yield).

Reduction of carboxylic acids to form alcohols is a key synthetic transformation for pharmaceutical and fine-chemical industries as well as for biomass conversion.^[1] Conventionally, this reaction has been performed by stoichiometric amounts of strong reducing agents such as lithium aluminum hydride or lithium triethylborohydride.^[2] The use of these strong reductants has serious drawbacks in terms of reagent compatibility, poor atom economy and safety. Selective catalytic hydrogenation of carboxylic acids is a straight-forward and effective synthetic method to obtain alcohols because the conditions are mild and water is the sole byproduct.^[3] However, carboxylic acid groups are thermodynamically and kinetically stable owing to the low electrophilicity of the carbonyl carbon. Because of this feature, these substances are among the most difficult carbonyl substrates to hydrogenate.^[4] So much effort has been devoted to hydrogenation of carboxylic acids employing heterogeneous and homogeneous catalysts in order to tackle this difficult process, and consequently, some processes have become industrial viable.^[5] Although these processes have already been in practical use and there has been substantial progress in recent years,^[6] the required harsh conditions often lead to low selectivity to desired products. In particular, hydrogenation of aromatic rings occurs rather than hydrogenation of carboxylic acid groups when both moieties are present in substrates (**Scheme 1**).^[4] There are a few reports describing selective hydrogenation of carboxylic acids containing aromatic rings using heterogeneous catalysts (Ru and Sn co-loaded Al₂O₃ catalysts).^[7] In these reports, however, the substrate scope is

limited to one example, and thus, the system lacks the generality. Recently, a biocatalytic system has been found to promote the selective hydrogenation of carboxylic acids.^[8] Although this would be an interesting strategy, development of more general systems are desired. In this regard, more recently, several research groups described new homogeneous catalysts for selective hydrogenation reactions of carboxylic acids that contain aromatic rings.^[9] For example, Leitner et al. reported that Ru(triphos)(TMM) (triphos = tridentate phosphine; TMM = trimethylene methane) can promote selective hydrogenation reaction of benzoic acid to benzyl alcohol.^[9a] Also, Beller et al. used Ru(acac)₃(triphos) (acac = acetylacetonate) as a homogeneous catalyst in the presence of a Lewis acid to promote the selective hydrogenation reaction for various carboxylic acids.^[9b] Saito et al. utilized a Ru^[9c] and Re^[9d] complexes as homogeneous catalysts for this process. A homogeneous Co-complex, comprised of Co(BF₄)₂·6H₂O and a triphos ligand, was developed by Bruin et al for promoting selective catalytic hydrogenation of carboxylic acids to the corresponding alcohols.^[9e] These processes represent important contributions to the synthesis of alcohols. In all cases, however, homogeneous catalysts were utilized that generally suffer from product separation and catalyst recycling. From the viewpoint of sustainable chemistry and large-scale applications, catalyst employed for this selective hydrogenation reaction should be heterogeneous and readily recyclable.

In the investigation described below, we uncovered a general and versatile heterogeneous catalytic system, comprised of TiO₂-supported Re (Re/TiO₂), which promotes selective alcohol forming hydrogenation reactions of carboxylic acids that contain aromatic and aliphatic moieties (**Scheme 1**). Unlike previously-developed catalysts, TiO₂-supported Re has the advantage of being heterogeneous and, therefore, it can be readily recovered and recycled. Moreover, the catalyst is easily prepared by using a facile impregnation method. The new



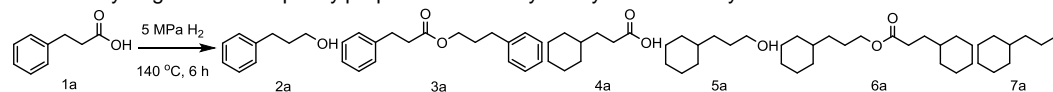
Scheme 1. Methods for hydrogenation of carboxylic acids containing aromatic ring(s).

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Supporting information for this article is given via a link at the end of the document.

Table 1. Hydrogenation of 3-phenylpropionic acid catalyzed by various catalyst.^a

Entry	Catalyst	Conv. [%]	Yield [%]					
			2a	3a	4a	5a	6a	7a
1	Re/TiO ₂	100	60	40	0	0	0	0
2	Pt/TiO ₂	100	0	0	0	64	34	1
3	Ir/TiO ₂	96	18	34	14	1	16	7
4	Ru/TiO ₂	59	0	6	45	0	6	0
5	Rh/TiO ₂	100	0	0	65	0	20	4
6	Pd/TiO ₂	91	0	0	90	0	0	0
7	Ag/TiO ₂	4	0	0	0	0	0	0
8	Cu/TiO ₂	1	0	0	0	0	0	0
9	Ni/TiO ₂	0	0	0	0	0	0	0
10	Co/TiO ₂	0	0	0	0	0	0	0
11	TiO ₂	0	0	0	0	0	0	0

^aReaction conditions: 2 mol% catalyst, 1 mmol phenylpropionic acid, no solvent, 5 MPa H₂, 140 °C, 6 h. Conversion and yields were determined by using GC with n-dodecane as an internal standard.

^bThe reaction was performed after calcination at 500 °C in the air. Full data for the catalyst screening are given in the Supporting Information.

catalyst displays high activity under relatively mild conditions and it does not require the use of additives. Density functional theory (DFT) calculations suggest that high affinity of Re toward -COOH group is an origin of the high selectivity for alcohol formation without promoting hydrogenation of aromatic rings. Finally, the broad carboxylic acid substrate scope of the process promoted by Re/TiO₂ makes it ideally suited for use in synthetic organic chemistry.

The Re/TiO₂ catalyst was synthesized by using a facile impregnation method employing NH₄ReO₄ (Aldrich) and TiO₂ (JRC-TIO-8 supplied from Catalysis Society of Japan). Typically, 0.72 g of NH₄ReO₄ was added to a glass vessel (500 ml) with 100 ml of deionized water (concentration of Re = 0.027 mol/l). After sonication for 1 minute to completely dissolve NH₄ReO₄, TiO₂ (9.5 g) was added to the solution and kept stirring for 15 min with 200 rpm at room temperature. This was followed by evaporation to dryness at 50 °C, and by drying at 90 °C under ambient pressure for 12 h. The prepared material was calcined at 500 °C in air for 3 h. For each experiment, the active catalysts were prepared by reduction in a Pyrex tube under a flow of H₂ (20 cm³ min⁻¹) at 500 °C for 0.5 h. Various characterization techniques were utilized to gain insight into structural features of Re/TiO₂. **Figure S1** shows the temperature programmed H₂-reduction (H₂-TPR) profile of Re-loaded TiO₂ after calcination. Inspection of the profile shows that large H₂ consumption occurred at around 300 °C corresponding to the reduction of the Re species. X-ray diffraction (XRD) patterns of calcined and reduced catalyst were found to be essentially identical, with peaks arising from TiO₂ being the only ones observed (**Fig. S2**). Energy dispersive x-ray (EDX) as well as transmission electron microscope analyses were performed to evaluate the element dispersion and particle size of Re in the Re/TiO₂ catalyst (**Fig.**

S3 and S4). The results of EDX analysis show that Re is present and that it is highly dispersed over the entirety of the TiO₂ particles. In addition, TEM measurements show that Re clusters on TiO₂ have 1-2 nm sizes, suggesting that they are highly dispersed on TiO₂.

In the initial phase of this effort, hydrogenation reactions of 3-phenylpropionic acid (**1a**) were used to screen the properties of various catalysts. Reactions were carried out using 1 mmol of **1a** and 2 mol% of the catalysts in a stainless autoclave (10 cm³) under 5 MPa H₂ at 140

°C for 6 h, following pretreatment of the catalyst with H₂ at 500 °C. The results of this study, summarized in **Tables 1 and S1** (Supporting Information), show that the Re/TiO₂ produced 3-phenylpropanol (**2a**) and the corresponding ester (**3a**). **3a** was formed via an esterification reaction of the starting carboxylic acid by the formed alcohol. On the contrary, low yields of the alcohol and ester were observed when other precious metal (Pt, Ir, Ru, Rh and Pd) containing catalysts were employed (**entries 2-6**). This was caused by competitive formation of products produced via dearomatization of benzene ring such as 3-cyclohexyl-propionic acid (**4a**), 3-cyclohexyl-propan-1-ol (**5a**) and 3-cyclohexyl-propionic acid 3-cyclohexyl-propyl ester (**6a**) and/or over-reduction to the alkane such as propyl-cyclohexane (**7a**). Ag-, Cu-, Ni-, Co-loaded TiO₂ catalysts did not promote the reduction reaction (**entries 7-10**). In addition, no reaction took place when TiO₂ was used as the catalyst (**entry 11**). It was also found that Re/TiO₂ gave **2a** and **3a** much more efficiently than other Re-based catalysts on other supports (**entries 13-22 in Table S1** in the Supporting Information). Also, NH₄ReO₄ as well as non-supported Re metal and its oxides (ReO₂ and Re₂O₇) were not effective catalysts for this hydrogenation reaction (**entries 23-26 in Table S1**). The results of the screening study clearly demonstrate that the combination of Re as the catalytically active species and TiO₂ as the support leads to a catalyst that effectively promotes selective alcohol forming hydrogenation reactions of carboxylic acids without formation of the undesired products such as alkanes and dearomatized compounds.

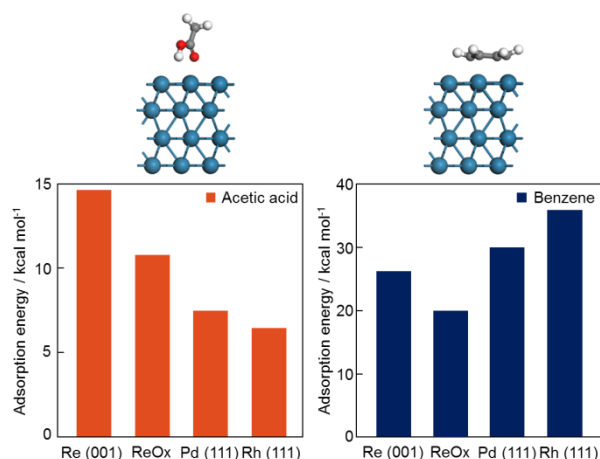


Figure 1. Adsorption energies of acetic acid (left) and benzene (right) on Re (001), ReOx, Pd (111) and Rh (111). Most stable adsorption structures of acetic acid and benzene adsorbed on Re (001) are shown (Side view).

In order to identify the origin of the high selectivity of the Re/TiO₂ catalyst toward alcohol formation over dearomatization of benzene ring, DFT calculations were conducted (See Supporting Information for detailed computational methods). Inspired by a report describing that the product selectivity in nitrostyrene hydrogenation depends strongly on relative adsorption affinity of its functional groups,^[10] adsorption affinity of –COOH and benzene moieties with catalyst surfaces were investigated by employing acetic acid and benzene as probe molecules. In addition to Re, metals promoting hydrogenation of aromatic rings rather than carboxylic acid groups such as Pd and Rh were examined for comparison. Moreover, partly oxidized Re (ReOx) was also modelled by adsorbing an oxygen atom on the metal surface and investigated in the same manner since oxidized Re species could be catalytically active sites.^[11] Note that most stable and common planes for each metal were utilized for this investigation. Most stable adsorption structures of benzene and acetic acid adsorbed on Re (001), ReOx, Pd (111) and Rh (111) surfaces are displayed in **Figure S5 and S6**, respectively. As demonstrated in **Fig. 1**, adsorption energies of benzene on Re (001) and ReOx are lower than those on Pd (111) and Rh (111). In contrast, adsorption energies of acetic acid on Re (001) and ReOx are higher than those on Pd (111) and Rh (111). Namely, Re and ReOx have relatively high affinity with –COOH groups compared to Pd and Rh, whereas the Re-based surfaces have lower affinity with benzene moiety in comparison with the other metal surfaces, indicating that Re has oxophilic nature.^[12] This relatively high affinity of Re toward –COOH could be one reason to explain the high selectivity of Re/TiO₂ for hydrogenation of 3-phenylpropionic acid.

The Re/TiO₂ catalyst system and reaction conditions for hydrogenation of 3-phenylpropionic acid were further optimized. Particularly, the effects of Re loading, pretreatment temperature and H₂ pressure were explored. The results given in **Table S3-5** show that catalytic activity reached a maximum when a 5 wt.% Re loading was utilized. The yields of the alcohol **2a** and ester **3a** increased with an increase in the pretreatment temperature

and H₂ pressure, which level at around 500 °C and 5 MPa, respectively. Note that **2a** yield was only 3% when the reaction was performed after calcination at 500 °C in the air without H₂ reduction as a pretreatment (**entry 12 in Table S1**). From the results of the effect of the H₂ reduction temperature, Re species having low valence states including metallic Re would be catalytically active sites for the hydrogenation reaction although it is difficult to identify the exact catalytically active sites for the hydrogenation reaction at the current time. Taking these observations into consideration, a Re loading of 5 wt.%, pretreatment temperature of 500 °C and H₂ pressure of 5 MPa were employed as optimized conditions.

The time course of the hydrogenation reaction of 3-phenylpropionic acid, carried out under the optimized conditions, is given in **Fig. 2**. Inspection of the profile shows that 3-phenylpropanol (**2a**) was efficiently generated from 3-phenylpropionic acid (**1a**) via a pathway involving initial formation of 3-phenylpropyl 3-phenyl-propionate (**3a**). Note that **3a** was formed as an intermediate product by esterification of **1a** and **2a**. The yield of **2a** reached 97% after 24 h. 3-Phenylpropionaldehyde, an anticipated intermediate in the process, along with over-reduced products were not observed even after 24 h. The reaction was also performed on a 10 times larger scale (i. e., 10 mmol **1a**) under the optimized conditions, as shown in **Scheme 2**. Column chromatographic separation of the crude product mixture gave **2a** in an isolated yield of 87%, indicating high scale-up potential of this catalytic process. Moreover, recycling test of Re/TiO₂ was performed to show its potential use as a recyclable heterogeneous catalyst. Following the reaction carried out, the catalyst was separated, washed with isopropanol, dried in air and then reused for an ensuing reaction. The desired alcohol was obtained in excellent yield for the 2nd run (97%). This is the same yield obtained for the 1st

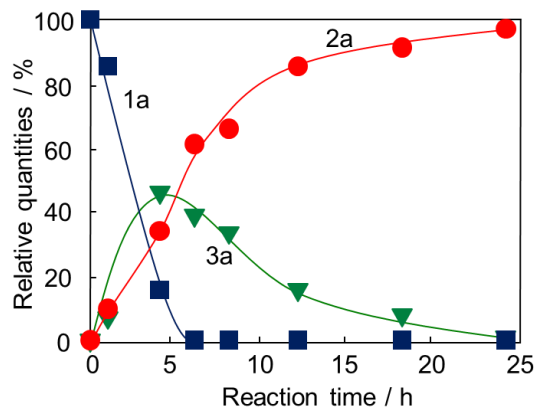
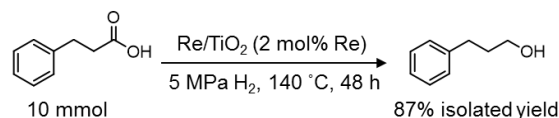


Figure 2. Time course of the hydrogenation reaction of 3-phenylpropionic acid catalyzed by Re/TiO₂. Substances in the plot are 3-phenylpropionic acid (**1a**), 3-phenylpropanol (**2a**) and 3-phenylpropyl 3-phenyl-propionate (**3a**).



Scheme 2. Gram scale synthesis of 3-phenylpropanol through hydrogenation of 3-phenylpropionic acid over Re/TiO₂.

Table 2. Hydrogenation of various carboxylic acids catalyzed by Re/TiO₂.^a

Entry	Substrate	Product alcohol	T [°C]	Yield [%]	
				Alcohol ^b	Ester
1			140	97 (94)	2
2			140	94 (91)	6
3			140	93 (90)	0
4			140	93 (86)	0
5			160	90 (84)	8
6			160	93 (86)	4
7			160	92 (83)	2
8			160	94 (88)	2
9			160	91 (87)	4
10			160	97 (93)	0
11			160	87 (80)	2
12			160	95 (83)	0
13			180	87 (84)	2
14 ^c			180	96 (82)	2

^aReaction conditions: 2 mol% Re, 1 mmol substrate, no solvent, 5 MPa H₂, 24 h. Conversion and yields were determined by using GC with n-dodecane as an internal standard. ^bIsolated yields are shown in parentheses. ^cThe reaction was performed for 36 h.

run, indicating that the Re/TiO₂ catalyst is recyclable. Note that the recycling reaction was carried out after H₂ reduction as is the case with the 1st run. If the H₂ reduction was not performed, the alcohol yield was 60%, indicating that the catalyst needs to be reduced for recycling. In order to further confirm heterogeneous nature of Re/TiO₂, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out. The result

indicates that 0.1% of the loaded Re (0.002 mol% of Re with respect to the reaction substrate) was leached after the 24 h reaction. In addition, a leaching test was performed, as shown in **Figure S7**. Specifically, we observed that removal of the catalyst following a 3 h period caused the hydrogenation reaction to cease, indicating only supported-Re species acts as a catalytically active site.

The substrate scope of the reaction was explored in order to show the potential versatility of the Re/TiO₂ catalyzed hydrogenation process. The results given in **Table 2** show that the catalytic system was capable of promoting alcohol forming hydrogenation reactions of a wide range of aromatic and aliphatic carboxylic acids. Although some substrates such as sterically hindered substrates displayed lower reactivity (**entries 6 and 9 in Table 2**), the use of increased reaction temperature in these cases leads to high alcohol yields. Notably, the substrate containing a chlorine-substituted benzene ring did undergo the selective hydrogenation reaction without change on the chlorine group (**entry 10 in Table 2**). Moreover, the Re/TiO₂-catalyzed system was applicable to the hydrogenation of substrates containing heterocyclic compounds to yield the corresponding alcohols (**entries 11 and 13 in Table 2**). At present, some limitations of the process do exist. For instance, olefin moieties were reduced under the reaction conditions (**entry 8 in Table 1**). However, the high chemoselectivity of the Re/TiO₂-catalyzed hydrogenation reaction and its concurrent compatibility with aromatic rings are features rarely seen with both homogeneous and heterogeneous hydrogenation catalysts although there are more number of papers for the selective hydrogenation of carboxylic acid derivatives such as esters^[13] and amides.^[14]

Driven by the desire to replace fossil fuel sources, much attention has been given to the conversion of biomass materials into fuels and chemicals.^[15] Selective hydrogenation reactions of carboxylic acids are important methods used for this purpose because they can be employed to generate fatty alcohols, which are widely used in the production of surfactants, polymers and solvents.^[16] To evaluate the applicability of the Re/TiO₂ catalyst to the goal of producing fatty alcohols, hydrogenation reactions of various fatty acids were explored. First, hydrogenation of lauric acid was conducted as a model reaction (**Table S6 and S7**, Supporting Information). Pretreatment temperature of 500 °C and H₂ pressure of 5 MPa were employed as optimized conditions as is the case with the above-described reactions. Further studies show that lauryl alcohol was produced in a 90% yield when the hydrogenation reaction was conducted using 5 MPa H₂ at 160 °C for 24 h (**Figure S8**). In addition, fatty acids bearing both long and short aliphatic chains did undergo efficient hydrogenation to produce the corresponding alcohols under these conditions (79-

99% alcohol yield), as shown in **Table S8**. These observations suggest that the catalytic system developed in this effort is applicable to bio-relevant carboxylic acid hydrogenation reactions.

In summary, we developed a heterogeneous catalytic system that promotes selective alcohol forming hydrogenation reactions of carboxylic acids under mild conditions without the need for additives. The Re/TiO₂ catalyst, which is readily prepared by using a facile impregnation method, could be utilized for selective hydrogenation of carboxylic acids that contain aromatic groups. DFT calculations suggest that the high selectivity for alcohol formation of the Re-based catalyst is originated from high affinity of Re with –COOH group over benzene ring. This finding would be a design guide to develop better catalysts for this process. Importantly, the catalyst was easily recyclable as a heterogeneous catalyst. In view of the importance of the process in both organic synthesis and industrial bulk chemical production, the new method for carboxylic acid hydrogenation should find wide utility and the findings should stimulate further studies targeted at the design of catalysts for selective hydrogenation reactions.

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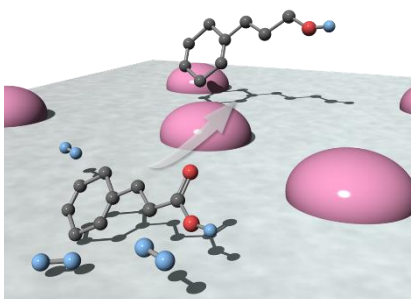
Keywords: Hydrogenation of carboxylic acid • Alcohol synthesis • Heterogeneous catalysis • Rhenium

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Entry for the Table of Contents

COMMUNICATION

TiO₂-supported Re (Re/TiO₂) has enabled selective catalytic hydrogenation of carboxylic acids having aromatic and aliphatic moieties to the corresponding alcohols under 5 MPa H₂ pressure at 140-180 °C. The Re/TiO₂ catalyst can be recyclable as a heterogeneous catalyst and demonstrate wide substrate scope with preparative useful yields.



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