HOKKAIDO UNIVERSITY

Title	TiO2-Supported Re as a General and Chemoselective Heterogeneous Catalyst for Hydrogenation of Carboxylic Acids to Alcohols
Author(s)	Toyao, Takashi; Siddiki, S. M. A. Hakim; Touchy, Abeda S. et al.
Citation	Chemistry-A European journal, 23(5), 1001-1006 https://doi.org/10.1002/chem.201604762
Issue Date	2017-01-23
Doc URL	https://hdl.handle.net/2115/67661
Rights	This is the peer reviewed version of the following article: Chemistry A European journal, 23(5), 2017-01-23, Pages 1001-1006, which has been published in final form at http://dx.doi.org/10.1002/chem.201604762. This article may be used for non-commercial purposes in accordance With Wiley-VCH Terms and Conditions for Self-archiving.
Type	journal article
File Information	Main text_Chem Eur J_2017.pdf



Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

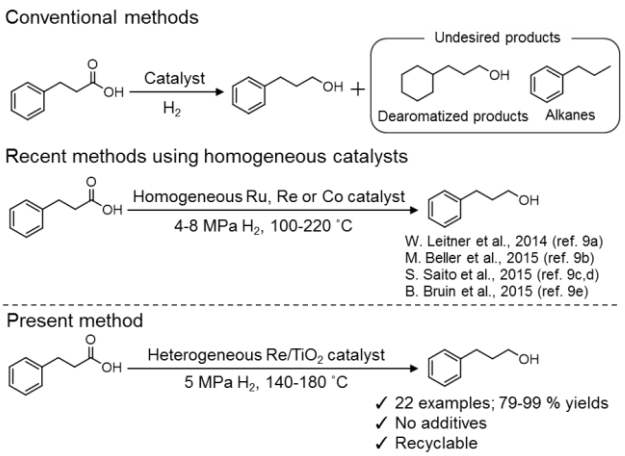
TiO_2-Supported Re as a General and Chemoselective Heterogeneous Catalyst for Hydrogenation of Carboxylic Acids to Alcohols

Takashi Toyao,*[a,b] S. M. A. H. Siddiki,[a] Abeda S. Touchy,[a] Wataru Onodera,[a] Kenichi Kon,[a] Yoshitsugu Morita,[c] Takashi Kamachi,[b, c] Kazunari Yoshizawa,[b, c] Ken-ichi Shimizu,*[a,b]

Abstract: TiO_2-supported Re, Re/TiO_2, has been found to promote selective hydrogenation of aromatic and aliphatic carboxylic acids to alcohols. Re/TiO_2 is superior to other transition metal-loaded TiO_2 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 H_2 at 140 ºC). Contrary to typical heterogeneous catalysts, Re/TiO_2 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 Al_2O_3 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 $Co(BF_4)_2{\cdot}6H_2O$ 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.

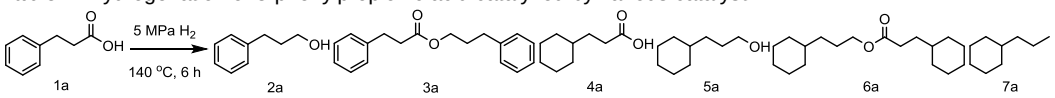
In the investigation described below, we uncovered a general and versatile heterogeneous catalytic system, comprised of TiO_2-supported Re (Re/TiO_2), which promotes selective alcohol forming hydrogenation reactions of carboxylic acids that contain aromatic and aliphatic moieties (**Scheme 1**). Unlike previously-developed catalysts, TiO_2-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).

[a] Dr. T. Toyao, Dr. S. M. A. H. Siddiki, Dr. A. S. Touchy, W. Onodera, Dr. K. Kon, Prof. Dr. K. Shimizu,
Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021 (Japan)
E-mail: toyao@cat.hokudai.ac.jp, kshimizu@cat.hokudai.ac.jp
[b] Dr. T. Toyao, Dr. T. Kamachi, Prof. Dr. K. Yoshizawa, Prof. Dr. K. Shimizu
Elements Strategy Initiative for Catalysis and Batteries, Kyoto University, Katsura, Kyoto 615-8520 (Japan)
[c] Dr. Y. Morita, Dr. T. Kamachi, Prof. Dr. K. Yoshizawa
Institute for Materials Chemistry and Engineering and International Research Center for Molecular Systems, Kyushu University, Fukuoka 819-0395 (Japan)
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

[a]Reaction conditions: 2 mol% catalyst, 1 mmol phenylpropionic acid, no solvent, 5 MPa H_2, 140 °C, 6 h. Conversion and yields were determined by using GC with n-dodecane as an internal standard. [b]The 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/TiO_2 makes it ideally suited for use in synthetic organic chemistry.

The Re/TiO_2 catalyst was synthesized by using a facile impregnation method employing NH_4ReO_4 (Aldrich) and TiO_2 (JRC-TIO-8 supplied from Catalysis Society of Japan). Typically, 0.72 g of NH_4ReO_4 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 NH_4ReO_4, TiO_2 (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 H_2 (20 cm^3 min^{-1}) at 500 °C for 0.5 h. Various characterization techniques were utilized to gain insight into structural features of Re/TiO_2. **Figure S1** shows the temperature programmed H_2-reduction (H_2-TPR) profile of Re-loaded TiO_2 after calcination. Inspection of the profile shows that large H_2 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 TiO_2 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/TiO_2 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 TiO_2 particles. In addition, TEM measurements show that Re clusters on TiO_2 have 1-2 nm sizes, suggesting that they are highly dispersed on TiO_2.

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 cm^3) under 5 MPa H_2 at 140 °C for 6 h, following pretreatment of the catalyst with H_2 at 500 °C. The results of this study, summarized in **Tables 1 and S1** (Supporting Information), show that the Re/TiO_2 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 TiO_2 catalysts did not promote the reduction reaction (**entries 7-10**). In addition, no reaction took place when TiO_2 was used as the catalyst (**entry 11**). It was also found that Re/TiO_2 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, NH_4ReO_4 as well as non-supported Re metal and its oxides (ReO_2 and Re_2O_7) 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 TiO_2 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.

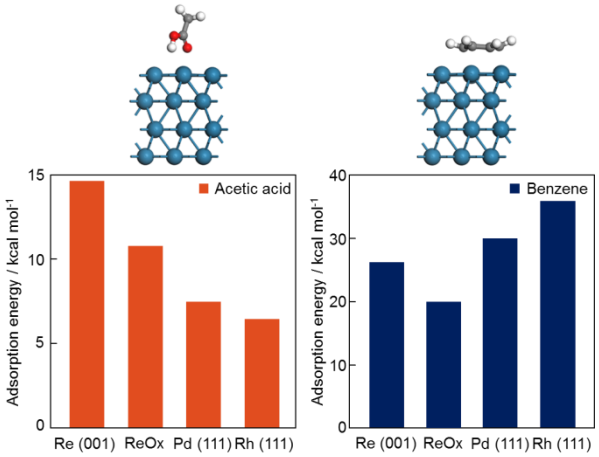


Figure 1. Adsorption energies of acetic acid (left) and benzene (right) on Re (001), ReOx, Pd (111) and Rh (111). Most stable adsorption structures of acetic acid and benzene adsorbed on Re (001) are shown (Side view).

In order to identify the origin of the high selectivity of the Re/TiO_2 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/TiO_2 for hydrogenation of 3-phenylpropionic acid.

The Re/TiO_2 catalyst system and reaction conditions for hydrogenation of 3-phenylpropionic acid were further optimized. Particularly, the effects of Re loading, pretreatment temperature and H_2 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 H_2 pressure, which level at around 500 ºC 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 H_2 reduction as a pretreatment (**entry 12 in Table S1**). From the results of the effect of the H_2 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 ºC and H_2 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/TiO_2 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

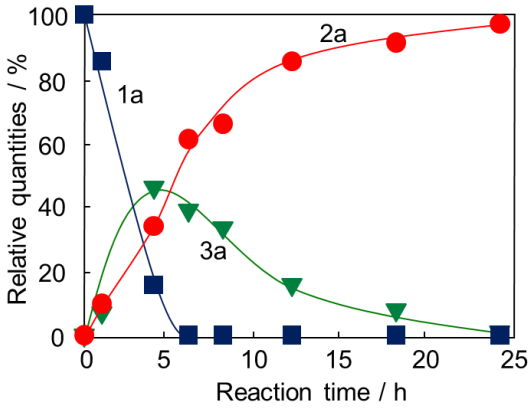
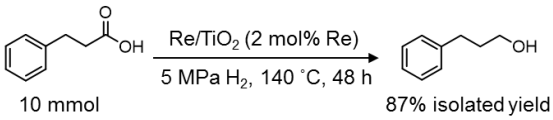
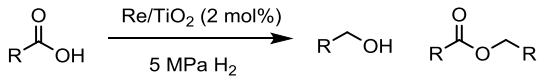


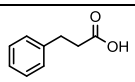
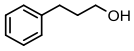
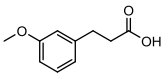
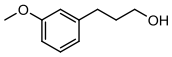
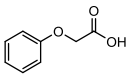
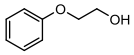
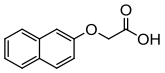
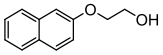
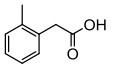
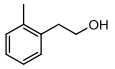
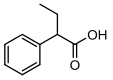
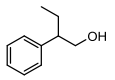
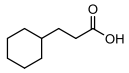
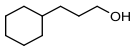
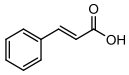
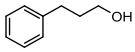
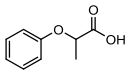
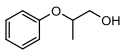
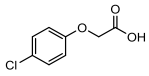
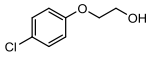
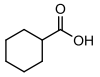
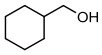
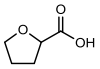
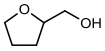
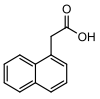
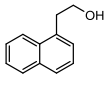
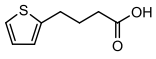
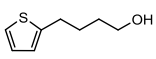
Figure 2. Time course of the hydrogenation reaction of phenylpropionic acid catalyzed by Re/TiO_2. Substances in the plot are 3-phenylpropionic acid (1a), 3-phenylpropanol (2a) and 3-phenylpropyl 3-phenyl-propionate (3a).



Scheme 2. Gram scale synthesis of 3-phenylpropanol through hydrogenation of phenylpropionic acid over Re/TiO_2.

Table 2. Hydrogenation of various carboxylic acids catalyzed by Re/TiO_2.[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

[a]Reaction conditions: 2 mol% Re, 1 mmol substrate, no solvent, 5 MPa H_2, 24 h. Conversion and yields were determined by using GC with n-dodecane as an internal standard. [b]Isolated yields are shown in parentheses. [c] The reaction was performed for 36 h.

run, indicating that the Re/TiO_2 catalyst is recyclable. Note that the recycling reaction was carried out after H_2 reduction as is the case with the 1st run. If the H_2 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/TiO_2, 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/TiO_2 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/TiO_2-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/TiO_2-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 hydrogenarion 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/TiO_2 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 ºC and H_2 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 H_2 at 160 ºC 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/TiO_2 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.

Acknowledgements

This work was supported by KAKENHI Grant numbers JP16H06595, JP26289299, JP24109014, JP15K13710 and JP15K05431 from Japan Society for the Promotion of Science (JSPS), the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) Projects of "Integrated Research on Chemical Synthesis" and "Elements Strategy Initiative to Form Core Research Center" and JST-CREST "Innovative Catalysts". TEM, STEM-EDX and ICP-AES analyses were carried out at the OPEN FACILITY, Hokkaido University.

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

[1] a) J. E. Carnahan, T. A. Ford, W. F. Gresham, W. E. Grigsby, G. F. Hager, *J. Am. Chem. Soc.* **1955**, *77*, 3766–3768; b) J. Magano, J. R. Dunetz, *Org. Process Res. Dev.* **2012**, *16*, 1156–1184; c) J. Pritchard, G. a. Filonenko, R. van Putten, E. J. M. Hensen, E. A. Pidko, *Chem. Soc. Rev.* **2015**, *44*, 3808–3833;d) C. Gunanathan, D. Milstein, *Chem. Rev.* **2014**, *114*, 12024–12087.

[2] a) A. B. Burg, H. I. Schlesinger, *J. Am. Chem. Soc.* **1937**, *59*, 780–787; b) W. G. Brown, *Org. React.* **1952**, *6*, 469–509; c) H. C. Brown, S. Krishnamurthy, *Tetrahedron* **1979**, *35*, 567–607; d) J. Seyden-Penne, Reductions by the Alumino- and Borohydrides in Organic Synthesis, 2nd ed.; Wiley: New York: 1997.

[3] a) H. S. Broadbent, G. C. Campbell, W. J. Bartley, J. H. Johnson, *J. Org. Chem.* **1959**, *24*, 1847–1854; b) M. Toba, S. Tanaka, S. Niwa, *Appl. Catal.A* **1999**, *189*, 243–250; c) F. M. A Geilen, B. Engendahl, M. H, W. Leitner, *J. Am. Chem. Soc.* **2011**, *133*, 14349–14358; d) P. A. Dub, T. Ikariya, *ACS Catal.* **2012**, *2*, 1718–1741; e) T. P. Brewster, A. J. M. Miller, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2013**, *135*, 16022–16025.

[4] D. He, N. Wakasa, T. Fuchikami, *Tetrahedron lett*. **1995**, *36*, 1059–1062.

[5] a) B. C. Trivedi, US4104478, **1978**; b) B. C. Trivedi, D. Grote, T. O. Mason, *J. Am. Oil Chem. Soc.* **1981**, *58*, 17–20; c) K. Yoshino, Y. Kajiwara, N. Takaishi, Y. Inamoto, J. Tsuji, *J. Am. Oil Chem. Soc.* **1990**, *67*, 21–24; d) R. Dostalek, R. Fischer, T. Krug, A. Paul, R. Pinkos, F. Stein, DE 1997156171, **1995**; e) A. Salvini, P. Frediani, M. Bianchi, F. Piacenti, L. Pistolesi, L. Rosi, *J. Organomet. Chem.* **1999**, *582*, 218–228; f) M. Toba, S. Tanaka, S. Niwa, F. Mizukami, Z. Koppány, *Appl. Catal. A Gen.* **1999**, *189*, 243–250; g) K. Tahara, JP 11199530, **1999**; h) Y. Hara, K. Endou, *Appl. Catal. A Gen.* **2003**, *239*, 181–195; i) H. G. Manyar, C. Paun, R. Pilus, D. W. Rooney, J. M. Thompson, C. Hardacre, *Chem. Commun.* **2010**, *46*, 6279–6281; j) L. Chen, Y. Li, X. Zhang, Q. Zhang, T. Wang, L. Ma, *Appl. Catal. A Gen.* **2014**, *478*, 117–128; k) L. Sandbrink, E. Klindtworth, H.-U. Islam, A. M. Beale, R. Palkovits, *ACS Catal.* **2015**, 677–680.

[6] a) A. Primo, P. Concepcio, A. Corma, *Chem. Commun.* **2011**, *47*, 3613–3615; b) Y. Takeda, Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.* **2012**, *2*, 2221–2223; c) M. Li, G. Li, N. Li, A. Wang, W. Dong, X. Wang, Y. Cong, *Chem. Commun.* **2014**, *50*, 1414–1416; d) Z. Liu, B. A. Tennant, J. L. Stavinoha, A. D. Messina, N. G. McMillan, US 20140121400, **2014**; e) K. Kandel, U. Chaudhary, N. C. Nelson, I. I. Slowing, *ACS Catal.* **2015**, *5*, 6719–6723; f) B. Rozmysłowicz, A. Kirilin, A. Aho, H. Manyar, C. Hardacre, J. Wärnå, T. Salmi, D. Y. Murzin, *J. Catal.* **2015**, *328*, 197–207.

[7] a) K. Tahara, E. Nagahara, Y. Itoi, S. Nishiyama, S. Tsuruya, M. Masai, *Appl. Catal. A Gen.* **1997**, *154*, 75–86; b) Z. Lv, Y. Song, Z. Zhu, J. Xie, S. Guo, CN 101096333, **2006**

[8] Y. Ni, P.-L. Hagedoorn, J.-H. Xu, I. W. C. E. Arends, F. Hollmann, *Chem. Commun.* **2012**, *48,* 2056–2058.

[9] a) T. Vom Stein, M. Meuresch, D. Limper, M. Schmitz, M. Holscher, J. Coetzee, D. J. Cole-Hamilton, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2014**, *136*, 13217–13225; b) X. Cui, Y. Li, C. Topf, K. Junge, M. Beller, *Angew. Chemie-Int. Ed.* **2015**, *54*, 10596–10599; c) M. Naruto, S. Saito, *Nat. Commun.* **2015**, *6*, 8140; d) S. Saito, R. Noyori, S. Agrawal, JP 2015-124156, **2015**; e) T. J. Korstanje, J. Ivar van der Vlugt, C. J. Elsevier, B. de Bruin, *Science* **2015**, *350*, 298–302.

[10] S. Furukawa, K. Takahashi, T. Komatsu, *Chem. Sci*. **2016**, *7,* 4476-4484.

[11] a) N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, *Angew. Chemie-Int. Ed.* **2014**, *2*, 1897–1900; b) S. Lwin, Y. Li, A. I. Frenkel, I. E. Wachs, *ACS Catal.* **2015**, *5,* 6807–6814; c) I. T. Ghampson, C. Sepulveda, R. Garcia, J. L. G. Fierro, N. Escalona, *Catal. Sci. Technol.* **2016**, *6*, 4356-4369.

[12] a) M. Chia, Y. J. Pag, D. Hibbitts, Q. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis, J. A. Dumesic, *J. Am. Chem. Soc.* **2011**, *133*, 12675–12689; b) B. K. Ly, B. Tapin, M. Aouine, P. Delichere, F. Epron, *ChemCatChem* **2015**, *7*, 2161–2178.

[13] a) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1998**, *3*, 1367–1368; b) K. Nomura, H. Ogura, Y. Imanishi, *J. Mol. Catal. A Chem.* **2001**, *166*, 345–349; c) L. A. Saudan, C. M. Saudan, C. Debieux, P. Wyss, *Angew. Chemie - Int. Ed.* **2007**, *46*, 7473–7476; d) S. Chakraborty, H. Dai, P. Bhattacharya, T. Neil, M. S. Gibson, J. A. Krause, H. Guan, N. T. Fairweather, *J. Am. Chem. Soc.* **2014**, *136*, 7869–7872; e) G. A. Filonenko, M. J. B. Aguila, E. N. Schulpen, R. van Putten, J. Wiecko, C. Müller, L. Lefort, E. J. M. Hensen, E. A. Pidko, *J. Am. Chem. Soc.* **2015**, *137*, 7620–7623; f) O. Ogata, Y. Nakayama, H. Nara, M. Fujiwhara, Y. Kayaki, *Org. Lett.* **2016**, *18*, 3894–3897.

[14] a) M. Ito, T. Ootsuka, R. Watari, A. Shiibashi, A. Himizu, T. Ikariya, *J. Am. Chem. Soc*. **2011**, *133*, 4240–4242; b) T. Miura, I. E. Held, S. Oishi, M. Naruto, S. Saito, *Tetrahedron Lett.* **2013**, *54*, 2674–2678; c) Y. Kita, T. Higuchi, K. Mashima, *Chem. Commun.* **2014**, *50*, 11211–11213; d) M.-L. Yuan, J.-H. Xie, S.-F. Zhu, Q.-L. Zhou, *ACS Catal.* **2016**, *6*, 3665–3669.

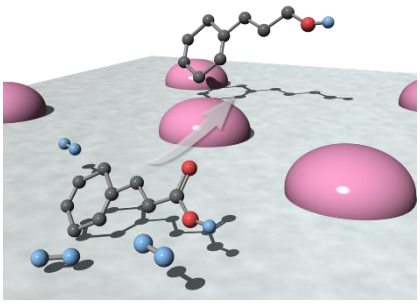
[15] a) M. J. Mendes, O. A. A. Santos, E. Jordão, A. M. Silva, *Appl. Catal. A Gen.* **2001**, *217*, 253–262; b) X. She, H. M. Brown, X. Zhang, B. K. Ahring, Y. Wang, *ChemSusChem* **2011**, *4*, 1071–1073; c) T. Mizugaki, Y. Nagatsu, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Green Chem.* **2015**, *17*, 5136–5139; d) Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, *ACS Catal.* **2015**, *5*, 7034–7047; e) L. Sandbrink, E. Klindtworth, H.-U. Islam, A. M. Beale, R. Palkovits, *ACS Catal.* **2015**, 677–680.

[16] a) S. Werkmeister, K. Junge, M. Beller, *Org. Process Res. Dev.* **2014**, *18*, 289−302; b) A. Suknev, V. Zaikovskii, V. Kaichev, E. Paukshtis, E. Sadovskaya, B. Bal'Zhinimaev, *J. Energy Chem.* **2015**, *24*, 646–654.

Entry for the Table of Contents

COMMUNICATION

TiO_2-supported Re (Re/TiO_2) has enabled selective catalytic hydrogenation of carboxylic acids having aromatic and aliphatic moieties to the corresponding alcohols under 5 MPa H_2 pressure at 140-180 °C. The Re/TiO_2 catalyst can be recyclable as a heterogeneous catalyst and demonstrate wide substrate scope with preparative useful yields.



Takashi Toyao, S. M. A. H. Siddiki, Abeda S. Touchy, Wataru Onodera, Kenichi Kon, Yoshitsugu Morita, Takashi Kamachi, Kazunari Yoshizawa, Ken-ichi Shimizu,**

Page No. – Page No.
TiO_2-Supported Re as a General and Chemoselective Heterogeneous Catalyst for Hydrogenation of Carboxylic Acids to Alcohols