

Electronic supplementary information for

## Selective hydrogenation of higher saturated carboxylic acids to alcohols using

### ReO<sub>x</sub>-Pd/SiO<sub>2</sub> catalyst

Yasuyuki Takeda, Yoshinao Nakagawa, Keiichi Tomishige

#### Details of procedures in catalyst preparation and reaction tests

The SiO<sub>2</sub> (G-6, BET surface area 535 m<sup>2</sup>/g) supplied by Fuji Silysia Chemical Ltd. was used as a support of the catalysts. The M/SiO<sub>2</sub> (M = Ir, Rh, Ru, Pt and Pd) catalysts were prepared by impregnating SiO<sub>2</sub> with an aqueous solution of H<sub>2</sub>IrCl<sub>6</sub> (Furuya Metals Co., Ltd), RhCl<sub>3</sub> · 3H<sub>2</sub>O (Soekawa Chemical Co., Ltd), RuCl<sub>3</sub> · nH<sub>2</sub>O (Kanto Chemical Co., Ltd.), H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O (Kanto Chemical Co., Ltd.) and PdCl<sub>2</sub> (Wako Pure Chemical Industries, Ltd.). After evaporating the solvent and drying at 383 K for 12 h, they were calcined in air at 773 K for 3 h. The M-ReO<sub>x</sub>/SiO<sub>2</sub> (M = Ir, Rh, Ru, Pt and Pd) was prepared by impregnating M/SiO<sub>2</sub> after the drying procedure with an aqueous solutions of NH<sub>4</sub>ReO<sub>4</sub> (Soekawa Chemical Co., Ltd). These were calcined in air at 773 K for 3 h after drying at 383 K for 12 h. The loading amount of Ir, Rh, Ru, Pt and Pd were 1 wt%. All the catalysts were used in powdery form with granule size of <100 mesh.

Activity test was performed in a 190-ml stainless steel autoclave with an inserted glass vessel. The calcined catalyst was put into an autoclave together with a spinner and a 5 wt% STA solution of 1,4-dioxane 20 g. After sealing the reactor, the air content was purged by flushing thrice with 1 MPa hydrogen. The autoclave was then heated to 413 K, and the temperature was monitored using a thermocouple inserted in the autoclave. After the temperature reached 413 K, the H<sub>2</sub> pressure was increased to 8 MPa. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After an appropriate reaction time, the reactor was cooled down. The autoclave contents were transferred to a vial, and the catalyst was separated by filtration. The standard conditions for the reaction were as follows: 413 K reaction temperature, 8 MPa initial hydrogen pressure, 4 h reaction

time, 1 g STA, 19 g 1,4-dioxane and 100 mg supported metal catalyst. The parameters were changed appropriately in order to investigate the effect of reaction conditions. Details of the reaction conditions are described in each result.

The products were analyzed using gas chromatography (Shimadzu GC-2025, GC-2014 and GC-17A) equipped with FID. A CP-Sil 5 capillary column (diameter 0.25 mm,  $\phi$  50 m) was used for higher fatty acids such as stearic acid, higher fatty alcohols such as (C<sub>n</sub>OH) 1-octadecanol, and high hydrocarbons (C<sub>n</sub>ane, C<sub>n</sub>-1ane) such as *n*-octadecane and *n*-heptadecane. A Porapak N (diameter 3.0 mm,  $\phi$  3.0 m) packed column was used for the separation of products in the gas phase such as CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. Products were also identified using GC-MS (QP5050, Shimadzu). We quantified stearic acid (STA), C<sub>n</sub> monohydroxy alcohol (C<sub>n</sub>OH), C<sub>n</sub> alkane (C<sub>n</sub>ane), CO<sub>2</sub>, methane and ethane. The conversion and the selectivity were defined on the carbon basis and defined as Eqs. (1) and (2).

$$\text{Conversion (\%)} = \frac{(\text{mol of substrate}) - (\text{mol of unreacted substrate})}{\text{mol of substrate}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\sum (\text{mol of the product})(\text{number of carbon atoms in the product molecule})}{(\text{mol of reacted substrate})(\text{number of carbon atoms in a substrate molecule})} \times 100 \quad (2)$$

The mass balance was also confirmed in each result and the difference in mass balance was always in the range of the experimental error (~5%). The data of reaction time dependence was based on the different runs using a fresh catalyst. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500). It was verified that the leaching of Re and Pd on ReO<sub>x</sub>-Pd/SiO<sub>2</sub> was negligible (<0.1%).

### Details of the temperature-programmed reduction

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector using 5% H<sub>2</sub> diluted with Ar (30 ml/min). The amount of catalyst was 0.05 g, and temperature was increased from room temperature to 1123 K at a heating rate of 10 K/min.

### Details of the optimization of the compositions of the $\text{ReO}_x\text{-Pd/SiO}_2$

Figure S1 shows the effect of support for  $\text{ReO}_x\text{-Pd}$  catalyst.  $\text{TiO}_2$ ,  $\text{CeO}_2$  and C gave low stearic acid conversion of <3%.  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  gave high conversion and high selectivity to C18OH. Among them,  $\text{SiO}_2$ -supported catalyst was most active, so we used  $\text{SiO}_2$  as a support.

Figure S2 shows the effect of the amount of Re over  $\text{ReO}_x\text{-Pd/SiO}_2$ .  $\text{Pd/SiO}_2$ , which was at  $\text{Re/Pd} = 0$ , showed no hydrogenation activity, indicating that the catalytic activity is generated by Re species. The activity of  $\text{ReO}_x\text{-Pd/SiO}_2$  increased with increasing Re/Pd ratio, and the high selectivity to C18OH was maintained. The STA conversion was almost saturated at  $\text{Re/Pd} \geq 10$ . In order to compare the activity per the amount of the active species, the turnover frequency (TOF) of the STA conversion was calculated on the basis of the amount of Re, and the results are also listed in Figure S1. In particular, in order to evaluate TOF more precisely, the comparison was carried out at shorter reaction time and lower conversion level. As a result,  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re/Pd} = 8$ , Pd 1 wt%) showed highest TOF ( $7.1 \text{ h}^{-1}$ ) at 2 h reaction time. For the comparison, the results of  $\text{ReO}_x/\text{SiO}_2$  with the same Re loading amount of  $\text{Re/Pd} = 8$  is also shown. The  $\text{ReO}_x/\text{SiO}_2$  showed lower TOF than  $\text{ReO}_x\text{-Pd/SiO}_2$ . The  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re/Pd} = 8$ , Pd 1 wt%) exhibited high hydrogenation activity than corresponding  $\text{ReO}_x/\text{SiO}_2$  and  $\text{Pd/SiO}_2$ , and it is concluded that the direct interaction between  $\text{ReO}_x$  and Pd generates high catalytic performance.

Figure S3 shows the effect of the loading amount of Pd over  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re} = 14 \text{ wt}\%$ ), where Re amount was fixed to that of  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re/Pd} = 8$ , Pd 1 wt%), in the STA hydrogenation. The promoting effect of Pd addition was observed at small amount such as 0.25 wt%. The activity was maximum at 1 wt% Pd, and too much Pd loading decreased the activity. The

result of the hydrogenation of methyl stearate using  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re/Pd} = 8$ , Pd 1 wt%). Here, the selectivity to products from STA is only shown, and products from methanol were excluded. It is verified that  $\text{ReO}_x\text{-Pd/SiO}_2$  catalyzed the hydrogenation of stearic acid ester to C18OH. However, the reactivity of methyl stearate was lower than that of STA, and the selectivity to C18OH from methyl stearate is not as high as that from STA, indicating that  $\text{ReO}_x\text{-Pd/SiO}_2$  is suitable in the hydrogenation of carboxylic acids, rather than in the hydrogenation of esters.

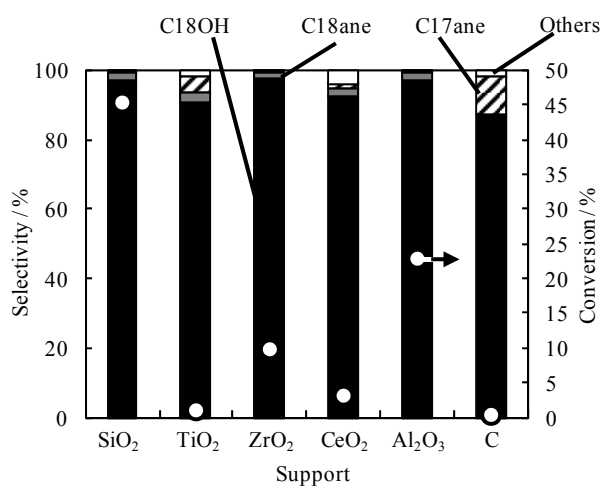


Fig. S1. Effect of support for ReO<sub>x</sub>-Pd catalyst.

Reaction conditions: 5 wt% STA solution in 1,4-dioxane 20 g, catalyst ReO<sub>x</sub>-Pd/support, Re/Pd=8, 1 wt%Pd, catalyst weight 0.1 g, H<sub>2</sub> pressure 8 MPa, temperature 413 K. STA: stearic acid, C18OH: 1-octadecanol, C18ane: *n*-octadecane, C17ane: *n*-heptadecane, Others: methane, ethane and CO<sub>2</sub>.

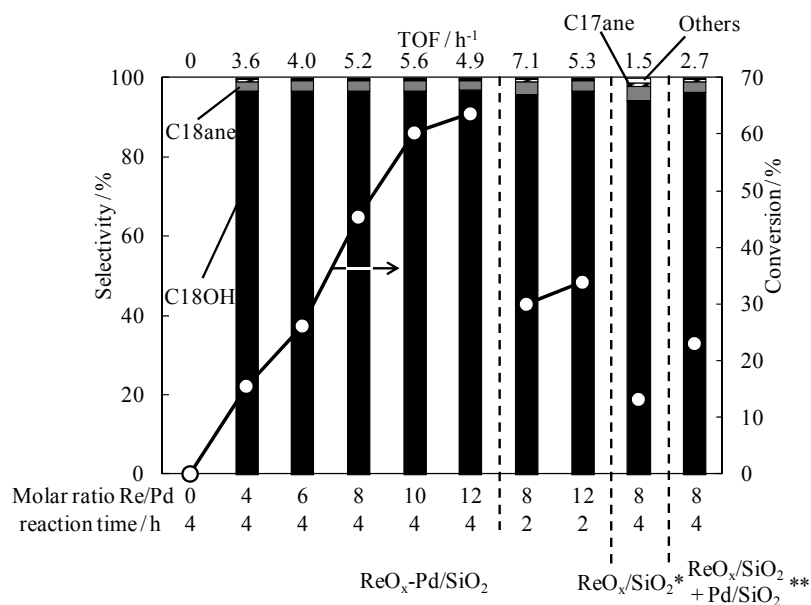


Fig. S2. Effect of the amount of Re over ReO<sub>x</sub>-1 wt%Pd/SiO<sub>2</sub> in the STA hydrogenation.

Reaction conditions: 5 wt% STA solution in 1,4-dioxane 20 g, catalyst weight 0.1 g, H<sub>2</sub> pressure 8 MPa,

temperature 413 K. TOF = (substrate (mol) \* Conversion / 100) / (Reaction time (h) \* Re amount (mol) ).

STA: stearic acid, C18OH: 1-octadecanol, C18ane: *n*-octadecane, C17ane: *n*-heptadecane, Others, methane, ethane and CO<sub>2</sub>.

\* The Re loading amount of ReO<sub>x</sub>/SiO<sub>2</sub> was the same as that of ReO<sub>x</sub>-Pd/SiO<sub>2</sub> (Re/Pd=8, Pd 1 wt%).

\*\* 0.1 g ReO<sub>x</sub>/SiO<sub>2</sub> + 0.1 g Pd/SiO<sub>2</sub> (Re/Pd = 8, Pd 1wt%) physical mixture.

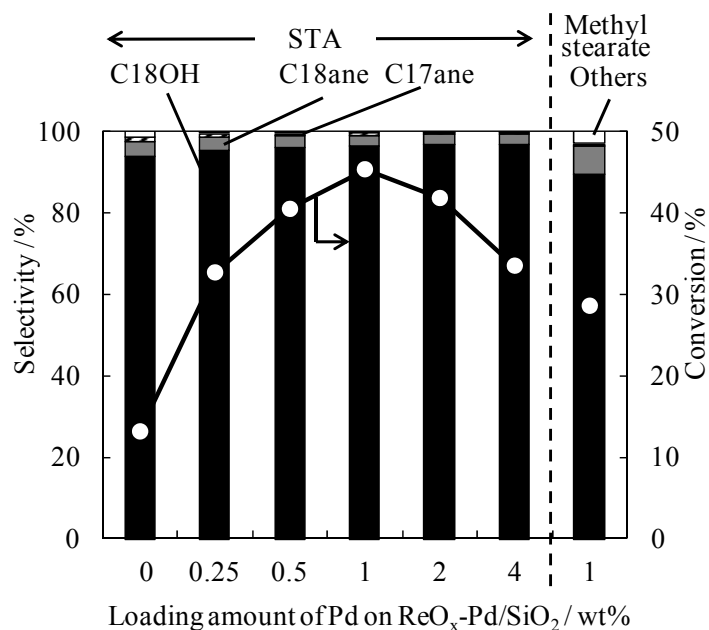


Fig. S3. Effect of the loading amount of Pd over  $\text{ReO}_x\text{-Pd/SiO}_2$  ( $\text{Re}=14$  wt%) in the STA hydrogenation and the result in hydrogenation of methyl stearate. Reaction conditions: 5 wt% STA solution in 1,4-dioxane 20 g, catalyst weight 0.1 g,  $\text{H}_2$  pressure 8 MPa, temperature 413 K, reaction time 4 h. STA: stearic acid, C18OH: 1-octadecanol, C18ane: *n*-octadecane, C17ane: *n*-heptadecane, Others: methane, ethane and  $\text{CO}_2$ .

\* Selectivity of methyl stearate hydrogenation was calculated with the exclusion of  $\text{C}_1$  products originated from methanol in the ester.

Table S1. List of reagents used in this study.

Reagent	purity grade	Supplier
1,4-dioxane	>99.5%	Wako Pure Chemical Industries, Ltd.
Stearic acid	>95.0%	Wako Pure Chemical Industries, Ltd.
1-octadecanol	>98.0%	Tokyo Chemical Industry Co., Ltd.
<i>n</i> -octadecane	>98.0%	Tokyo Chemical Industry Co., Ltd.
Palmitic acid	>95.0%	Wako Pure Chemical Industries, Ltd.
1-hexadecanol	>95.0%	Wako Pure Chemical Industries, Ltd.
<i>n</i> -hexadecane	>97.0%	Wako Pure Chemical Industries, Ltd.
Myristic acid	>98.0%	Wako Pure Chemical Industries, Ltd.
1-tetradecanol	>97.0%	Wako Pure Chemical Industries, Ltd.
Tetradecane	>99.0%	Wako Pure Chemical Industries, Ltd.
Lauric acid	>98.0%	Wako Pure Chemical Industries, Ltd.
1-dodecanol	>95.0%	Wako Pure Chemical Industries, Ltd.
Dodecane	>99.0%	Wako Pure Chemical Industries, Ltd.
Decanoic acid	>98.0%	Wako Pure Chemical Industries, Ltd.
1-decanol	>95.0%	Wako Pure Chemical Industries, Ltd.
Decane	>99.0%	Wako Pure Chemical Industries, Ltd.
Octanoic acid, from Palm	>98.0%	Wako Pure Chemical Industries, Ltd.
1-octanol	>98.0%	Wako Pure Chemical Industries, Ltd.
Octane	>98.0%	Wako Pure Chemical Industries, Ltd.
Hexanoic acid	>99.0%	Wako Pure Chemical Industries, Ltd.
1-hexanol	>97.0%	Wako Pure Chemical Industries, Ltd.
Hexane	>96.0%	Wako Pure Chemical Industries, Ltd.
Methyl stearate	>95.0%	Tokyo Chemical Industry Co., Ltd.