Supplementary Material (ESI) for Chemical Communications

Chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol

Shuichi Koso[a], Ippei Furikado[a], Akira Shimao[a], Tomohisa Miyazawa[a], Kimio Kunimori[a], and Keiichi Tomishige[a,b*]

Electronic supplementary information

Details of procedures in catalyst preparation and reaction tests

A Rh/SiO_2 catalyst was prepared by impregnating SiO_2 with an aqueous solution of $RhCl_3 \cdot 3H_2O$. The SiO_2 (G-6 BET surface area 535 m^2/g) was supplied by Fuji Silysia Chemical Ltd. After the impregnation procedure and drying at 383 K for 12 h, the catalyst was calcined in air at 773 K for 3 h. Rh-ReO_x/SiO_2 was prepared by impregnating Rh/SiO_2 after the drying procedure with an aqueous solution of NH_4ReO_4. These precursors were supplied from Soekawa Chemical Co., Ltd. ReO_x/SiO_2 was also prepared by impregnating SiO_2 with a aqueous solution of the same precursors as the case of Rh-ReO_x/SiO_2. It was calcined in air at 773 K for 3 h after drying at 383 K for 12 h. The loading amount of Rh was 4 wt% and that of Re was in the range of 0.25-1.0 by the molar ratio of Re to Rh. Ru/C and Raney Ni catalysts were supplied from Wako Pure Chemical Industries Ltd. The loading amount of Ru was 5 wt%. Copper chromite was supplied from Aldrich Chemical Co. Inc. All catalysts were used in powdery form with granule size of < 100 mesh.

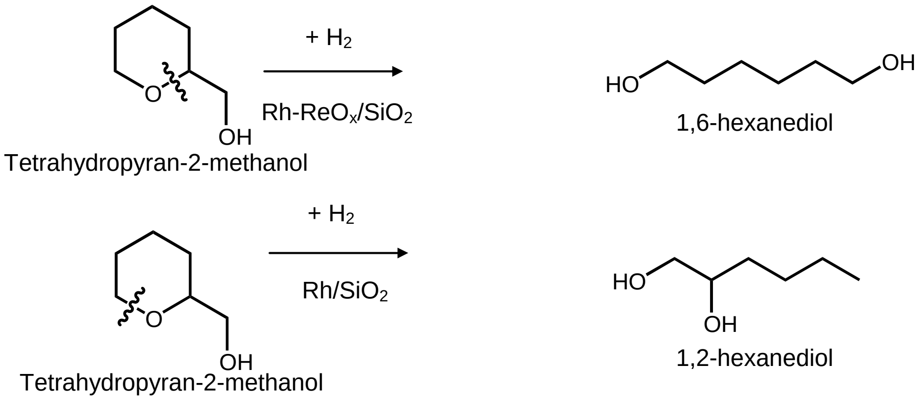
Catalytic testing was performed in a 190 ml stainless steel autoclave with an inserted glass vessel. An aqueous solution of a reactant was placed into the autoclaves together with an appropriate amount of catalyst and spinner. After sealing the reactors, their air contents were purged by flushing three times with 1 MPa hydrogen (99.99%; Takachiho Chemical Industrial Co. Ltd.). Autoclaves were then heated to the required temperature and pressurized to 1 MPa for the reduction pretreatment. After 1 h, the H_2 pressure was increased to 8 MPa. The experiment was stopped after an appropriate reaction time. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After stopping the experiment, the reactors were cooled down and all gases were collected in a gas bag. The autoclave contents were transferred to vials and the catalysts were separated by centrifugation and filtration.

In the case of the hydrogenolysis of tetrahydrofurfuryl alcohol, 20 ml of 5 wt% aqueous solution was used and tetrahydrofurfuryl alcohol was commercially available from Wako Pure Chemical Industries Ltd. with purities greater than 98%. In the reaction, l,5-pentanediol (1,5-PeD), 1,2-pentanediol (1,2-PeD), and

1-pentanol (1-PeOH) were mainly produced, and 2-methyltetrahydrofuran and 2-pentanol (2-PeOH) were also detected. In addition, various cracking products are also formed by the cracking of carbon-carbon bond in the molecule. Consequently, the sum of the cracking products, 2-methyltetrahydrofuran and 2-pentanol is represented by “Others” in Table 1. Analyses of products were carried out using a gas chromatograph equipped with a flame ionization detector (FID) (Rtx®-1 PONA capillary column, 0.25 mmϕ 100 m, GC-17A; Shimadzu Corp.). The yield of the products were determined by the external standard method using an aqueous solution of each product with known concentration. The mass balance was checked by comparing between amount of products and that of unreacted reactants. A small amount of methane as a gaseous product was detected, and it is included in “Others”. In addition, the agreement in terms of the mass balance indicated that polymeric by-products were not formed.

In the case of the hydrogenolysis of tetrahydrofuran, 20 ml of 5 wt% tetrahydrofuran aqueous solution was used, and tetrahydrofuran was commercially available from Wako Pure Chemical Industries Ltd. with purities greater than 99.5%. As a product of the reaction, 1-butanol was only detected. Experimental apparatus and reaction procedures are the same as the case of tetrahydrofurfuryl alcohol.

In the case of the hydrogenolysis of tetrahydropyran-2-methanol, 10 ml of 5 wt% tetrahydropyran-2-methanol aqueous solution was used, and tetrahydropyran-2-methanol was commercially available from Aldrich Chemical Co. Inc. with purities greater than 98%. As a product of the reaction, 1,6-hexanediol, 1,2-hexanediol, 1-hexanol and 2-hexanol were mainly detected. Experimental apparatus and reaction procedures are the same as the case of tetrahydrofurfuryl alcohol. The reaction scheme of the hydrogenolysis of tetrahydropyran-2-methanol is described in Scheme S1.



Scheme S1. Reaction routes in the hydrogenolysis of tetrahydropyran-2-methanol.

Details of the ICP analysis

The amount of metal leaching was measured by an inductively-coupled plasma (ICP) (Nippon Jarrell-Ash ICAP-575) of the solution after the reaction. The Re leaching ratio to the total Re on the catalyst was determined to about 5%, which is as small as Re/Rh=0.025. On the other hand, the Rh leaching amount was below the detection limit of the ICP analysis, and the leaching ratio to the total Rh on the catalyst is < 0.1% and the leaching of Rh was negligible.

Details of the CO adsorption measurement

The amount of CO chemisorption was measured in a high-vacuum system using a volumetric method. Before adsorption measurements, the catalysts were treated in H_2 at 393 K for 1 h. Subsequently, the adsorption was performed at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The sample weight was about 0.1 g. The dead volume of the apparatus was about 60 cm^3. Adsorption amount of CO is represented as the molar ratio to Rh and this corresponds to the number of the surface atoms assuming that the stoichiometry of adsorbed CO to surface Rh atom is one, which can be catalytically active sites.

Details of the TEM observation

Transmission electron microscope (TEM) images were taken for determination of the particle size using equipment (JEM 2010; JEOL) operated at 200 kV. The catalysts after the reaction were used as a sample for the TEM observation. Supersonic waves dispersed the sample in 2-propanol. The samples were placed on Cu grids under air atmosphere. The average particle size (d_s) was calculated by $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (d_i, particle size; n_i, number of particles with d_i).(S1) Figure S1 shows a TEM image of the used Rh-ReO_x/SiO_2 (Re/Rh=0.5), and dark spots are assigned to metal particles. The average particle size was estimated to be 4.3±0.3 nm. On the other hand, The average particle size of Rh/SiO_2 was determined to be 3.5±0.3 nm.(S2)

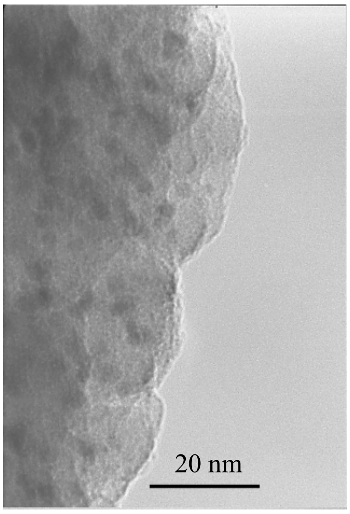


Figure S1. TEM image of Rh-ReO_x/SiO_2 (Re/Rh=0.5) after the reaction.

Details of the X-ray diffraction patterns

X-ray diffraction (XRD) patterns were obtained in a Philips X'pert diffractometer. Cu Kα (λ = 0.154 nm, 45 kV, 40 mA) radiation was used as X-ray source. XRD patterns of reduced catalysts were collected under air atmosphere. The particle size on Rh-ReO_x/SiO_2 and Rh/SiO_2 were calculated by the Scherrer's equation.(S3)

Details of the X-ray absorption spectroscopic analysis

Re L_3-edge EXAFS and Re L_3-edge XANES were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2008B1235). The storage ring was operated at 8.0 GeV. A Si (111) single crystal was used to obtain a monochromatic X-ray beam. Measurements were carried out in a similar way to the reference. (S4) For the curve fitting analysis, the empirical phase shift and the amplitude function for the Re-O and Re-Re bonds were extracted from data of NH_4ReO_4 and Re powder, respectively. Theoretical functions for the Re-Rh bond were calculated using the FEFF8.2 program.(S5) Analyses of EXAFS and XANES data were performed using a computer program (REX2000 Ver. 2.3.3; Rigaku Corp.).

The Re L_3-edge EXAFS results of Rh-ReO_x/SiO_2 (Re/Rh=0.5) before and after the reaction and the curve fitting results are shown in Figure S2. The catalyst before the reaction corresponds to that after the reduction at 393 K. The EXAFS analysis of the catalyst after the reaction indicates the presence of Re-O, Re-Re and Re-Rh bonds (Table 2). Although it is not possible to propose the model structure at present, the direct interaction between Rh surface and Re species is detected clearly. In addition, the coordination number of the Re-O bond on Rh-ReO_x/SiO_2 after the reaction was much smaller than that on NH_4ReO_4 precursor. In addition, the EXAFS of the catalyst before the reaction is almost the same as that after the reaction. This indicates that the Re species is reduced during the reduction pretreatment. Figure S3 shows the Re L_3-edge XANES spectra. The first peak is the L_3-edge XANES is called as a white line, and the white line intensity L_3-edge XANES is known to be an informative indication of electronic state. The larger white line intensity is due to greater electron vacancy in d-orbital.(S6-11) The white line intensity of the Rh-ReO_x/SiO_2 before and after the reaction was clearly smaller than that of NH_4ReO_4 precursor, and larger than that of Re metal. This comparison indicates that the Re species on Rh-ReO_x/SiO_2 in the reaction is partially reduced, which is also supported by the EXAFS result. Based on the EXAFS and XANES analysis, it is suggested that the ReO_x cluster species are located on the surface of Rh metal particles.

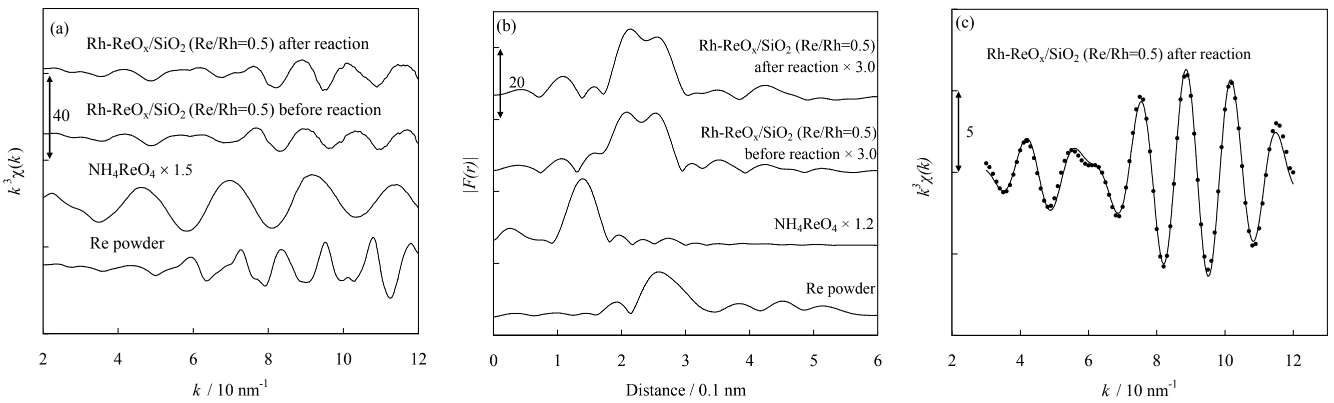


Figure S2. Results of Re L_3-edge EXAFS analysis of Rh-ReO$_x$/SiO$_2$ (Re/Rh=0.5) before and after the hydrogenolysis of tetrahydrofurfuryl alcohol.
(a) k^3-weighted EXAFS oscillations,
(b) Fourier transform of k^3-weighted Re L_3-edge EXAFS, FT range: 30-120 nm^{-1},
(c) Fourier filtered EXAFS data (solid line) and calculated data (dots),
Fourier filtering range: 0.129-0.301 nm

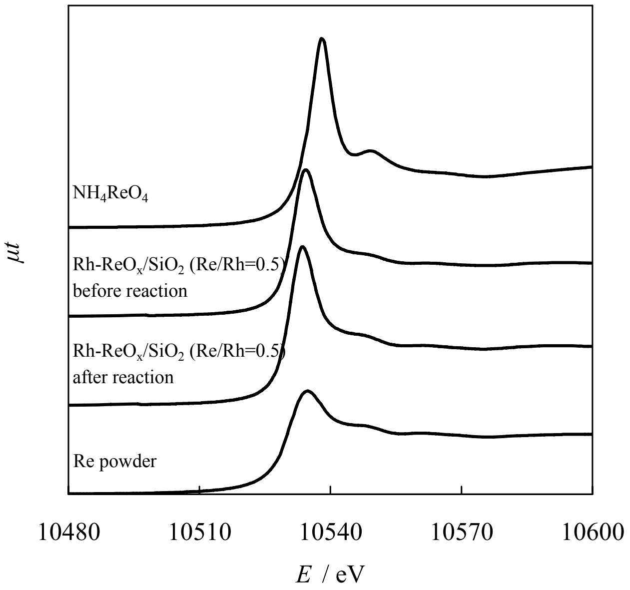


Figure S3. Results of Re L_3-edge XANES of Rh-ReO$_x$/SiO$_2$ before and after the hydrogenolysis of tetrahydrofurfuryl alcohol.

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