Supporting Information

Effect of Perimeter Interface Length between 2D WO_3 Monolayer Domain and γ-Al_2O_3 on Selective Hydrogenolysis of Glycerol to 1,3-Propanediol

Takeshi Aihara[a], Hiroki Miura[a,b,d], and Tetsuya Shishido[a,b,c,d*]

[a] Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

[b] Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

[c] Research Center for Gold Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

[d] Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8520, Japan

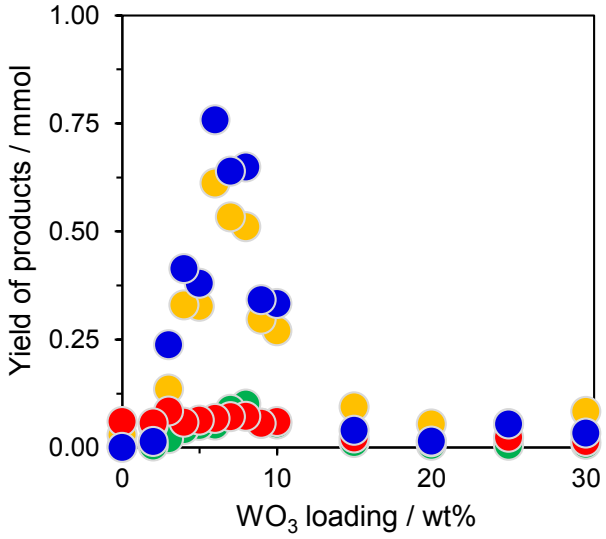
[*] Corresponding author: Tel: +81-42-677-2850 Fax: +81-42-677-2850 (T. Shishido)

E-mail address: shishido-tetsuya@tmu.ac.jp (T. Shishido)

Analytical data

Contents:

1. Effect of WO_3 loading on hydrogenolysis over $Pt/WO_3/Al_2O_3$ catalysts

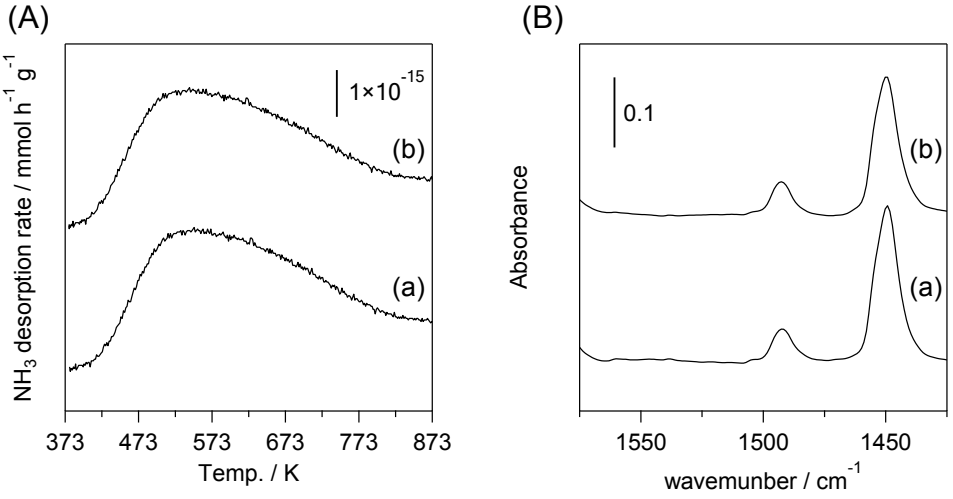


WO_3 loading	Yield / mmol				
/ wt%	Glycerol	1,3-Propanediol	1,2-Propanediol	1-PrOH	2-PrOH
30	2.53	0.03	0.01	0.08	0.01
25	2.67	0.05	0.02	0.05	0.00
20	2.81	0.02	0.01	0.05	0.01
15	2.72	0.04	0.02	0.09	0.01
10	2.19	0.33	0.06	0.27	0.05
9	1.95	0.34	0.06	0.30	0.06
8	1.45	0.65	0.07	0.51	0.10
7	1.31	0.64	0.07	0.53	0.09
6	1.38	0.76	0.07	0.61	0.05
5	1.97	0.38	0.06	0.33	0.05
4	2.07	0.41	0.06	0.33	0.04
3	2.23	0.24	0.08	0.14	0.02
2	2.83	0.01	0.06	0.05	0.00
0	2.88	0.00	0.06	0.03	0.00

Figure S1. Effect of WO_3 loading on hydrogenolysis over $Pt/WO_3/Al_2O_3$ catalysts. Conditions: Glycerol (3 mmol), Catalyst (100 mg), H_2O (9 mL), P_{H2}= 5 MPa, T= 453 K, t= 15 h. ●: 1,3-propanediol, ●: 1,2-propanediol, ●: 1-propanol, ●: 2-propanol.

2. Investigation of the surface acidity of $Pt/WO_3/Al_2O_3$ catalysts by NH_3-TPD and Pyridine adsorbed IR.

NH_3-TPD was carried out to estimate the acidity on the catalysts. The TPD was performed on a MicrotracBEL BELCAT-II in the following manners: 100 mg of catalyst was pretreated with He (50 mL min^{-1}) gas at 773 K for 1 h. The sample was cooled down to 373 K in He gas. Gaseous NH_3/He (5/45 mL min^{-1}) was adsorbed for 1 h and then removed in He gas for 1 h. Consecutively, TPD was started at 373 K, and the temperature was raised to 873 K at a ramping rate of 10 K min^{-1} under in the flowing He. The desorbed products were determined by using a BELMass and recorded on an online personal computer. All IR spectra were recorded using a FT-IR spectrometer (FT/IR-4200 typeA, JASCO, Hachioji, Tokyo, Japan) equipped with a TCD detector at 298 K. Each sample (30 mg) was pressed into a self-supporting wafer with a diameter of 20 mm. Catalysts were pretreated under 20 kPa of O_2 for 1 h at 773 K and then cooled with evacuation. To determine the amount of Brønsted and Lewis acid sites on catalysts, The catalyst was exposed to 0.5 kPa of flowing pyridine vapor at 298 K for 15 min and then evacuated at 423 K for 15 min.



Catalyst	Acidity / μmol g^{-1}		
	NH_3-TPD	Pyridine IR	
		(Brønsted)	(Lewis)
After reaction	158	0	143
Before reaction	137	0	156

Figure S2. (A) NH_3-TPD profiles of $Pt/WO_3/Al_2O_3$ with 20 wt% WO_3 loading catalysts. (B) IR spectrum of pyridine on $Pt/WO_3/Al_2O_3$ catalysts with 20 wt% WO_3 loading. (a) catalyst before reaction and (b) catalyst after reaction.

3. Effect of Pt dispersion on hydrogenolysis over $Pt/WO_3/Al_2O_3$ catalysts.

The Pt dispersion of the catalyst was measured by the CO pulse method at room temperature using an Okura BP-2 instrument (Okura Riken, Japan) with a thermal conductivity detector (TCD). Prior to CO adsorption, the catalyst was pre-treated with H_2 at 453 K for 1 h. The stoichiometric ratio of Pt/CO was assumed to be 1:1 for the calculation of the accessible surface Pt atoms on the catalysts.

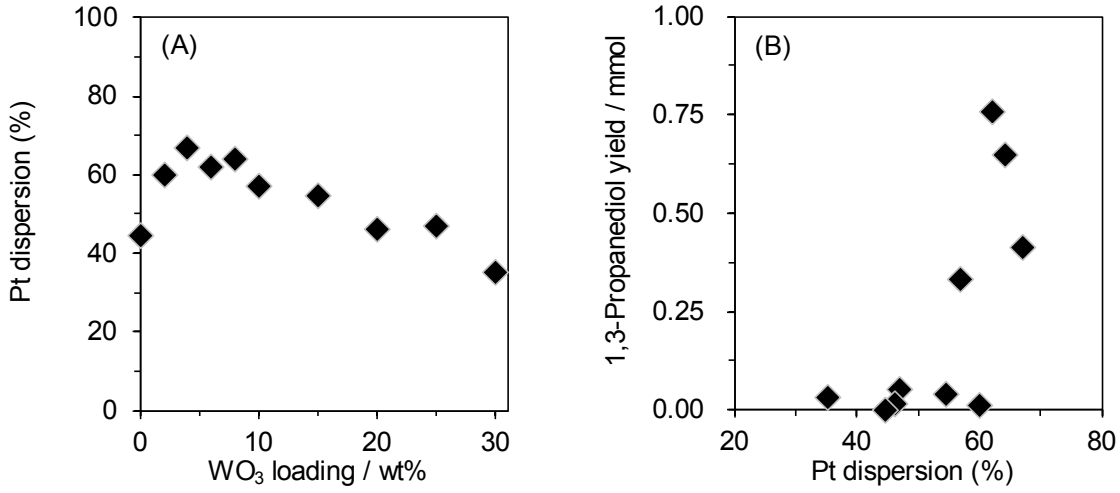


Figure S3. (A) Pt dispersion of $Pt/WO_3/Al_2O_3$ catalysts with various WO_3 loadings. (B) Effect of Pt dispersion on hydrogenolysis over $Pt/WO_3/Al_2O_3$ catalysts. Conditions: Glycerol (3 mmol), Catalyst (100 mg), H_2O (9 mL), P_{H2}= 5 MPa, T= 453 K, t= 15 h.

4. TEM image of WO_3/Al_2O_3 catalyst.

TEM images were recorded using a JEOL JEM-3200FS transmission electron microscope. The samples were prepared by depositing drops of ethanol suspensions containing small amounts of the powders onto carbon-coated copper grids (JEOL Ltd.) followed by evaporation of the ethanol in air.

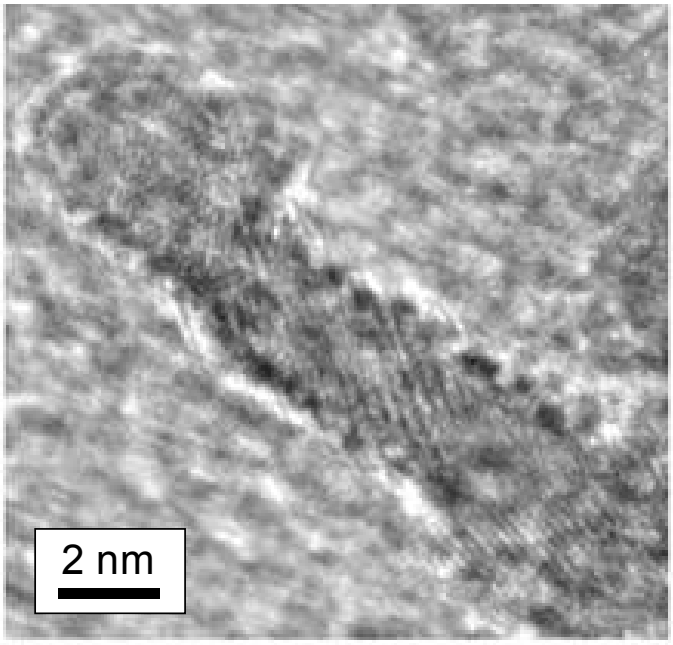


Figure S4. TEM image of WO_3/Al_2O_3 catalyst with 7 wt% WO_3 loading.

5. XP spectra of $Pt/WO_3/Al_2O_3$ and WO_3/Al_2O_3 catalysts with various WO_3 loadings in the W 4f region

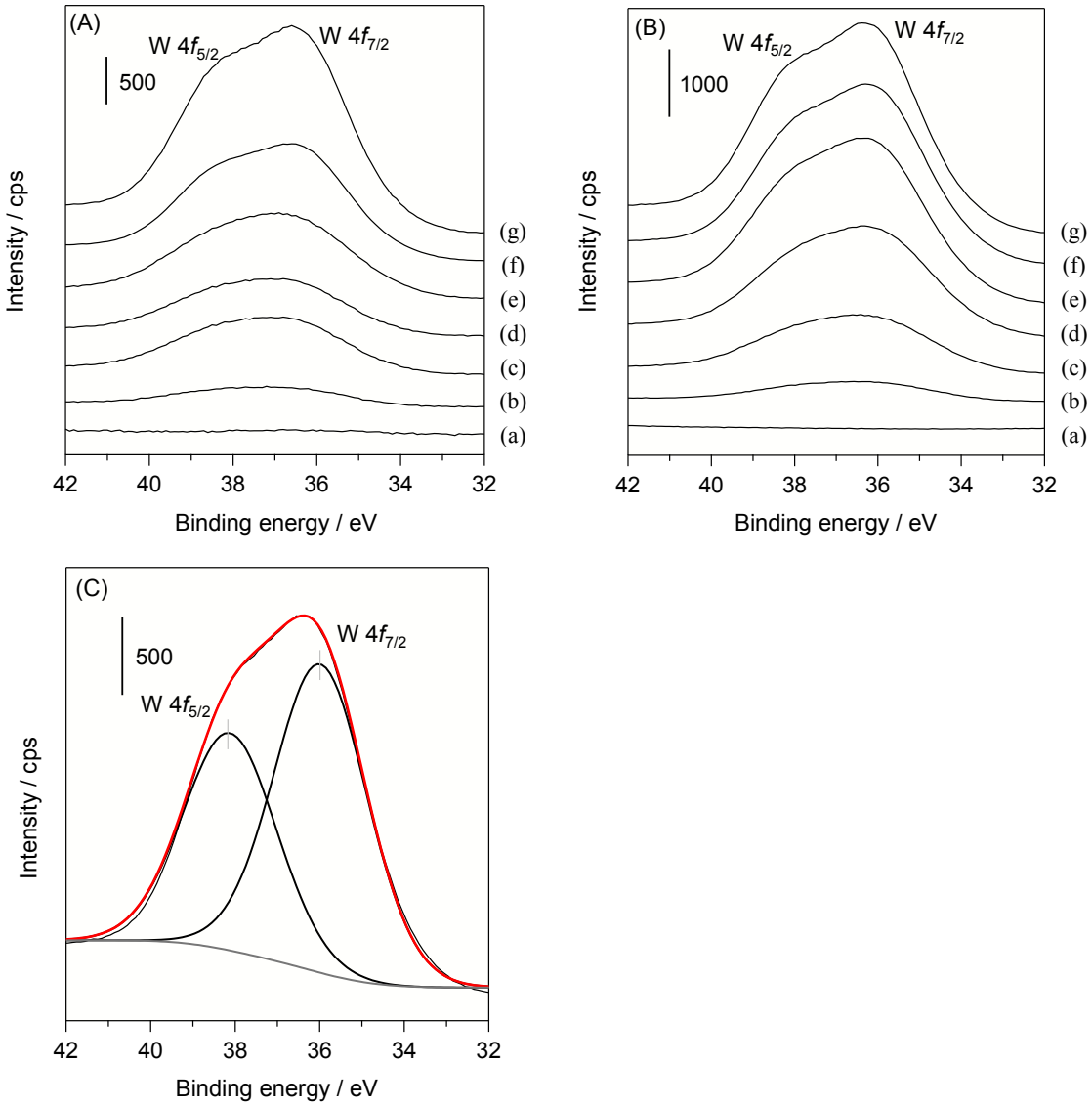


Figure S5. XP spectra of $Pt/WO_3/Al_2O_3$ (A) and WO_3/Al_2O_3 catalysts (B) with various WO_3 loadings in the W 4f region. (a) 0, (b) 2, (c) 6, (d) 10, (e) 15, (f) 20 and (g) 30 wt%. (C) Fitting result of $Pt/WO_3/Al_2O_3$ catalyst with 20 wt% WO_3 loading. ——: spectrum, ——: fitting function, — — —: peak 1, – – –: peak 2, ---: background.

6. Deconvolution of the W L_1-edge XANES spectra in $Pt/WO_3/Al_2O_3$ catalysts and reference samples

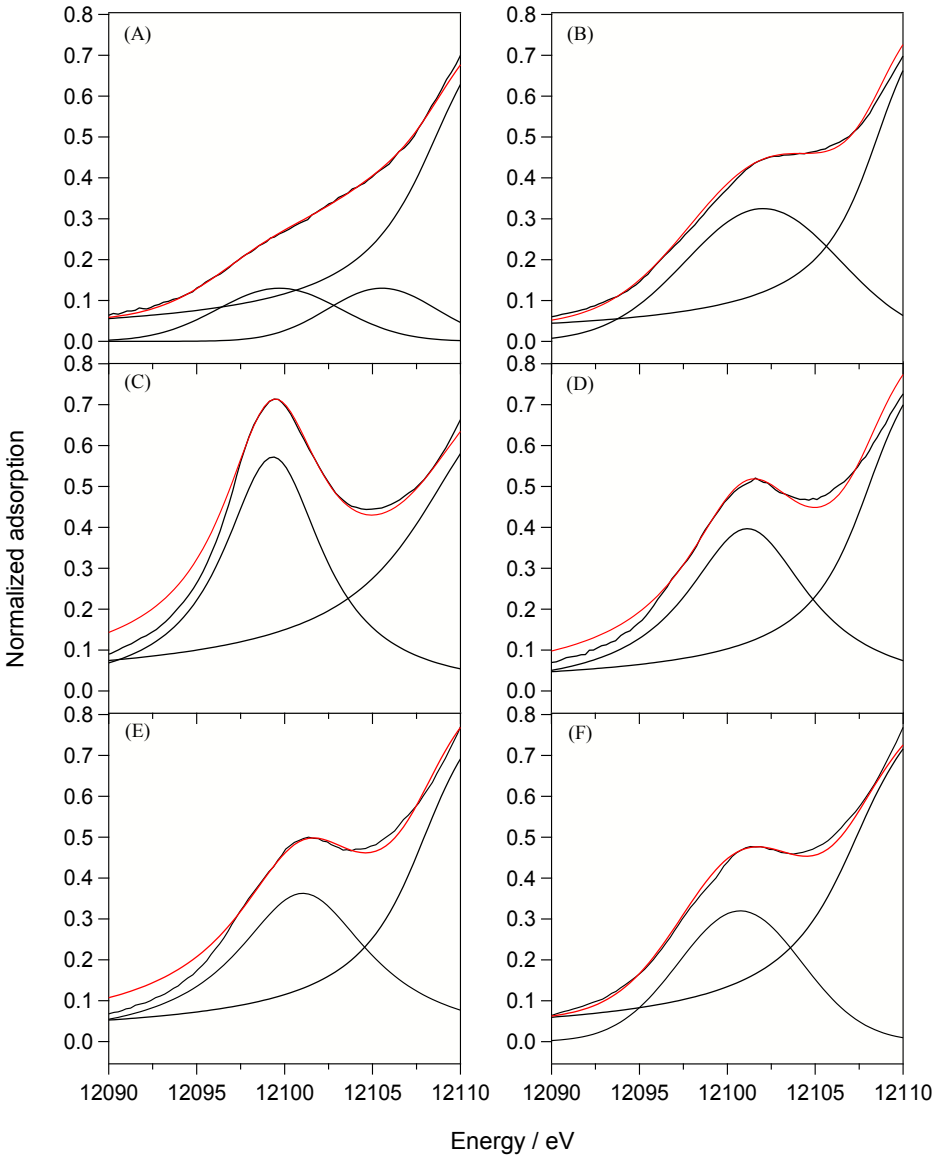


Figure S6. Deconvolution of the W L_1-edge XANES spectra in $Pt/WO_3/Al_2O_3$ catalysts and reference. (A) Ba_2NiWO_6, (B) *m*-WO_3, (C) Na_2WO_4, $Pt/WO_3/Al_2O_3$ with (D) 2, (E) 6 and (F) 20 wt% WO_3 loading. — –: spectrum, ——: fitting function, – – –: peak 1, — — —: peak 2, ---: background.

7. XP spectra of $Pt/WO_3/Al_2O_3$ before and after reduction in the W 4f region

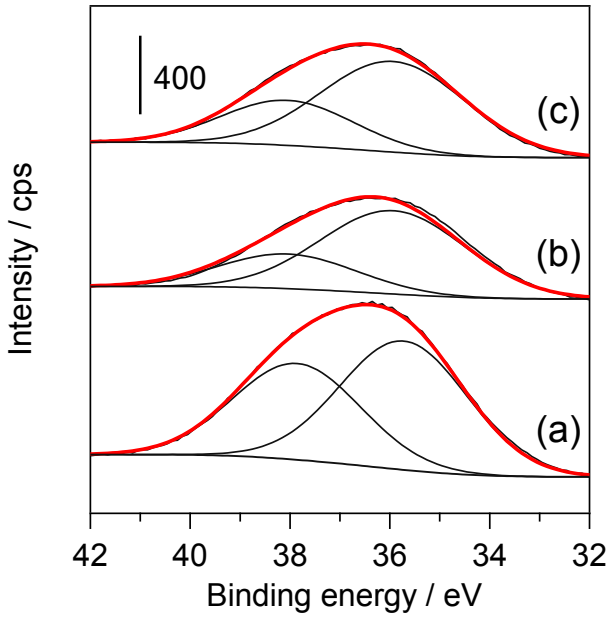


Figure S7. XP spectra of $Pt/WO_3/Al_2O_3$ catalysts with 20 wt% WO_3 loading. (a): Fresh, (b): Reduced at 453 K for 1 h under 5 MPaH_2 in H_2O, (c): Reduced at 573 K for 1 h under 0.1 MPaH_2. ——: spectrum, – – –: fitting function, — — —: peak 1, – – –: peak 2, – – –: background.