Regulating d-band center of Pt for highly effective H_2 storage through toluene hydrogenation at low temperatures

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Experimental details

1. Preparation of the $Pt(OH)_2/Al_2O_3$ precursors.

Typically, 300 mg of commercial γ-Al_2O_3 supports were dispersed in a 30 mL solution of $KPtCl_4$ (Pt: 3 mg) at room temperature for 1 h. After adding 200 mg of urea, the solution was heated to 70 °C for 4 h reaction under vigorous stirring. Finally, the $Pt(OH)_2/Al_2O_3$ precursors were washed for 4 times with distilled water and dried overnight at 60 °C.

2. Preparation of various Pt/Al_2O_3 catalysts

The **Pt/Al_2O_3-H** catalysts were obtained by reduction of the $Pt(OH)_2/Al_2O_3$ precursors at 300 °C for 2 h under 5% H_2/Ar atmosphere with a heating rate of 5 °C min^{-1}.

The **Pt/Al_2O_3-H-Air** catalysts were prepared by calcining Pt/Al_2O_3-H catalysts in air at 200 °C for 2 h with a heating rate of 5 °C min^{-1}.

The **Pt/Al_2O_3-F** catalysts were obtained by reduction of the $Pt(OH)_2/Al_2O_3$ precursors at room temperature with formaldehyde solution. Typically, 300 mg of the $Pt(OH)_2/Al_2O_3$ precursors were dispersed in a 30 mL solution of formaldehyde (30%) for 24 h. The Pt/Al_2O_3-F catalysts were washed for 4 times with distilled water and dried overnight at 60 °C.

The **Pt/Al_2O_3-F-H_2** catalysts were obtained by treating the Pt/Al2O3-F catalysts under 5% H_2/Ar at 300 °C for 2 h with a heating rate of 5 °C min^{-1}.

The **Pt/Al_2O_3-P** catalysts were obtained by treating the $Pt(OH)_2/Al_2O_3$ precursors in the mixture of methanol and H_2O with volume ratio of 1:9 at room for 2 h. The

preparation process was occurred under N_2 protection.

The Pt/Al_2O_3-B catalysts were obtained by treating the $Pt(OH)_2/Al_2O_3$ precursors with $NaBH_4$ solution. Typically, 300 mg of the $Pt(OH)_2/Al_2O_3$ precursors were dispersed in a 30 mL solution. Then, 5 mL of $NaBH_4$ solution (2 mg mL^{-1}) was added for 2 h reaction at room temperature. The Pt/Al_2O_3-B catalysts were washed for 3 times with distilled water and dried overnight at 60 °C.

3. Characterizations

Transmission electron microscope (TEM) were conducted with a Hitachi HT-7700 transmission electron microscope with an accelerating voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) spectra was acquired using a Thermo Electron Model K-Alpha with Al K_α as the excitation source. XRD analysis was performed using Bruker AXS, D8 Discover USA equipped with Cu K_α radiations.

4. Catalytic hydrogenation of toluene

Typically, 10 mg of catalysts were well dispersed in 14.2 mmol of toluene in a 500 mL autoclave, followed by three cycles of purging and washing using 1 MPa H_2. Subsequently, the catalytic reactions were conducted at desired temperatures and H_2 pressures. After the reaction, the autoclave was naturally cooled down. The liquid phase of reaction solution was analyzed by gas chromatograph.

The turnover frequency (TOF) values were calculated by the following equation:

$$TOF = \frac{n_0 \times C}{t \times n_{cat} \times D}$$

where n_0 is the molar mass of reactants, C is the conversion of reactants at the specific reaction time of t, n_{cat} is the molar mass of Pt atoms, t is the reaction time, and D is the dispersion of Pt atom.

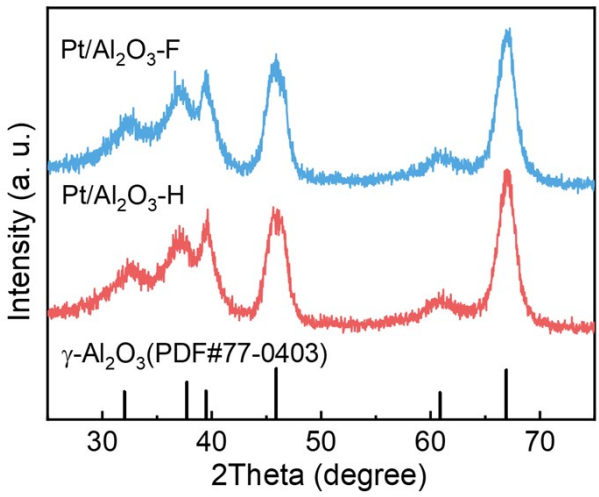

Figure S1. XRD patterns of the Pt/Al_2O_3-F and Pt/Al_2O_3-H catalysts.

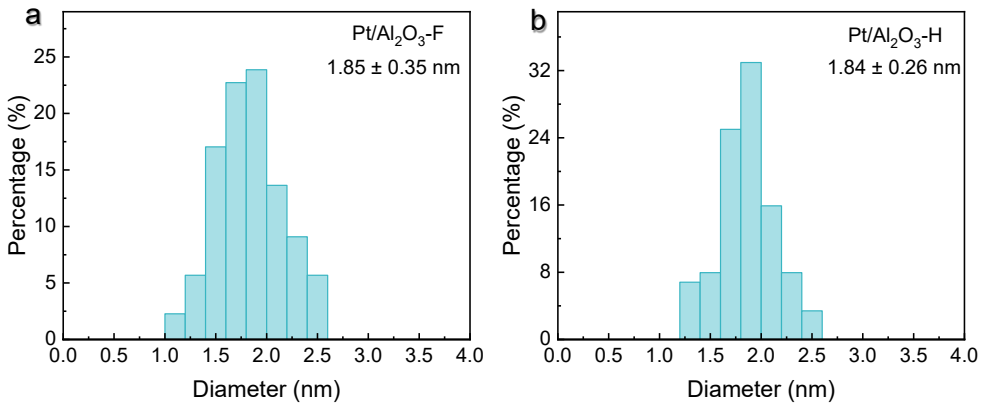

Figure S2. The size distribution of Pt nanoparticles on the (a) Pt/Al_2O_3-F and (b) Pt/Al_2O_3-H catalysts.

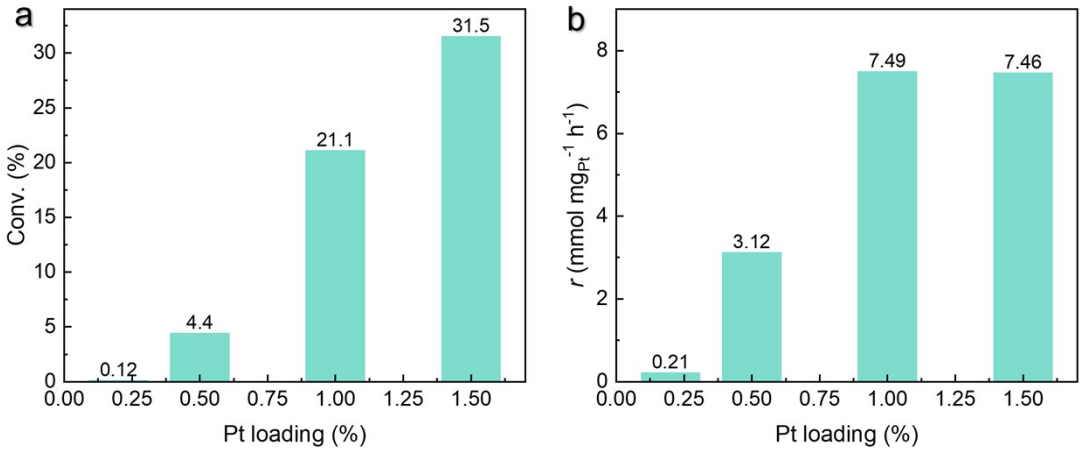

Figure S3. Catalytic performance of Pt/Al_2O_3-F with various Pt loading for toluene hydrogenation. (a) Conversion of toluene and (b) conversion rate of toluene based on the mass of unit Pt. **Reaction conditions:** toluene (14.2 mmol), catalysts (10 mg), 80 °C, 2 MPa H_2 and 2 h.

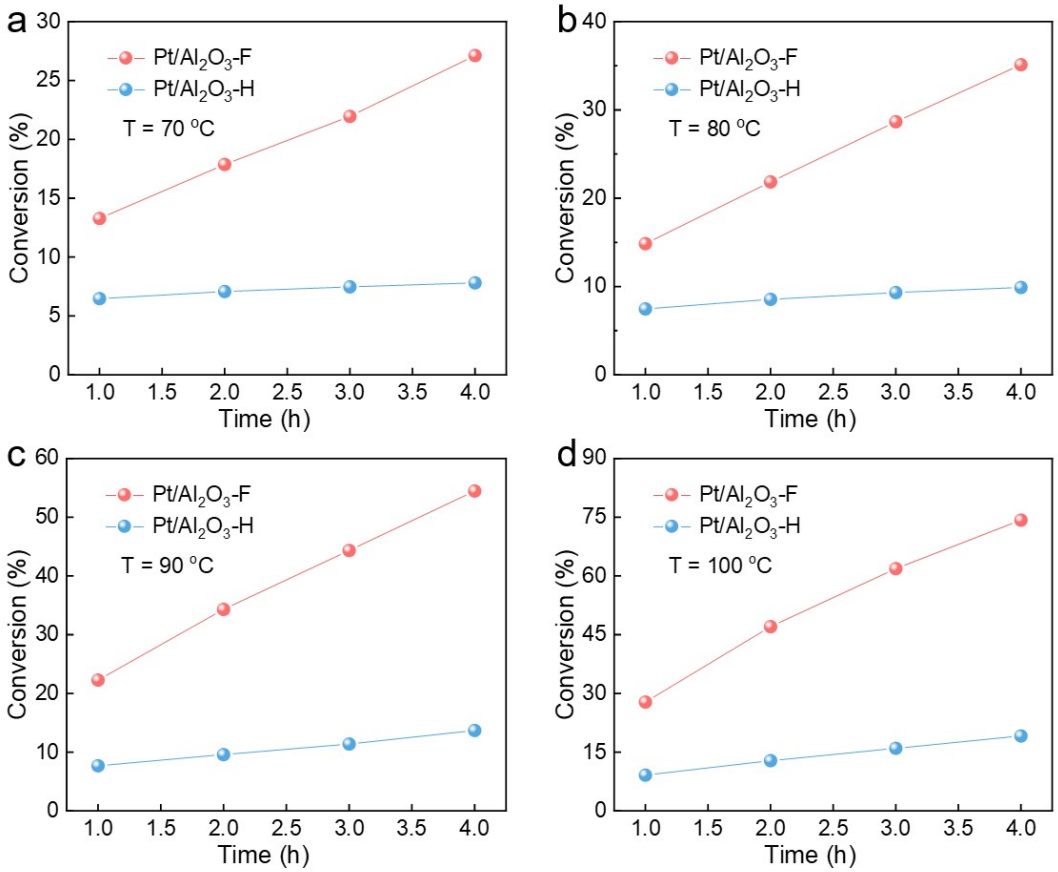

Figure S4. Catalytic performance of toluene hydrogenation at various reaction temperatures by Pt/Al_2O_3-F and Pt/Al_2O_3-H catalysts. **Reaction conditions:** toluene (14.2 mmol), catalysts (10 mg) and 2 MPa H_2.

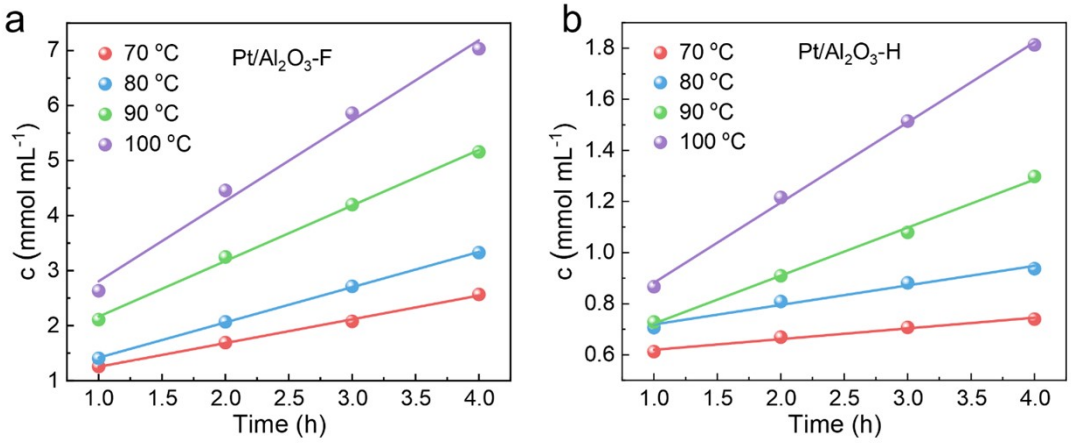

Figure S5. Molar mass of toluene as a function of reaction time at various temperatures catalyzed by Pt/Al_2O_3-F and Pt/Al_2O_3-H catalysts.

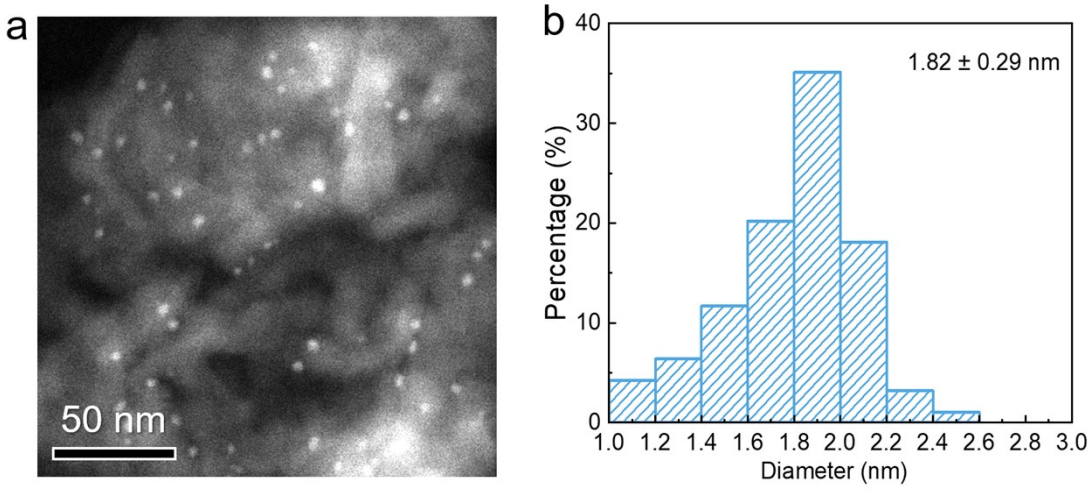

Figure S6. (a) Dark field TEM image and (b) size distribution of supported Pt nanoparticles for the used Pt/Al_2O_3-F catalysts.

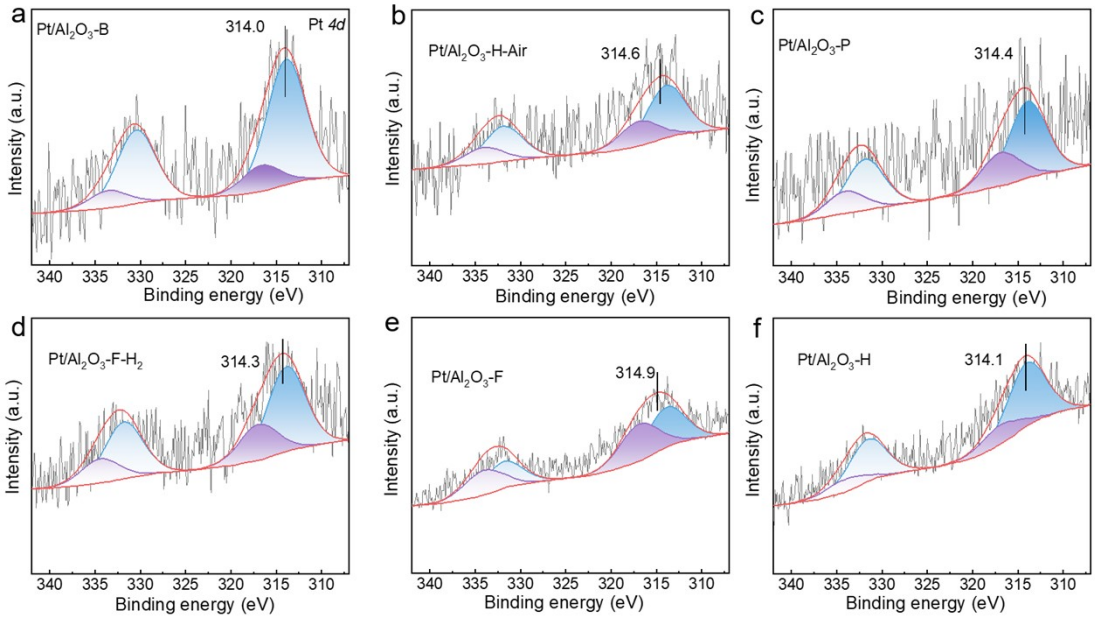

Figure S7. XPS analysis of Pt *4d* peaks for the (a) Pt/Al_2O_3-B, (b) Pt/Al_2O_3-H-Air, (c) Pt/Al_2O_3-P, (d) Pt/Al_2O_3-F-H_2, (e) Pt/Al_2O_3-F, and (f) Pt/Al_2O_3-H catalysts.

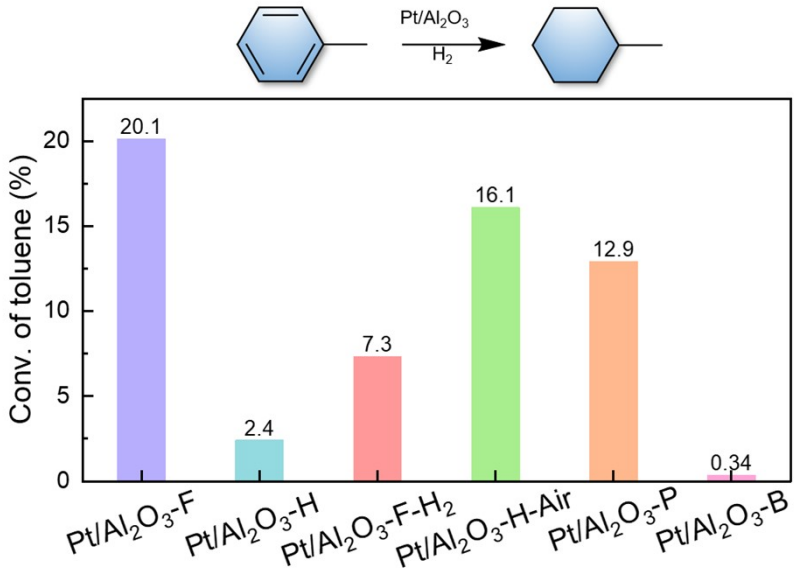

Figure S8. Catalytic activity of toluene hydrogenation catalyzed by various Pt/Al_2O_3 catalysts. **Reaction conditions:** toluene (14.2 mmol), catalysts (10 mg), 80 °C, 2 MPa H_2 and 2 h.

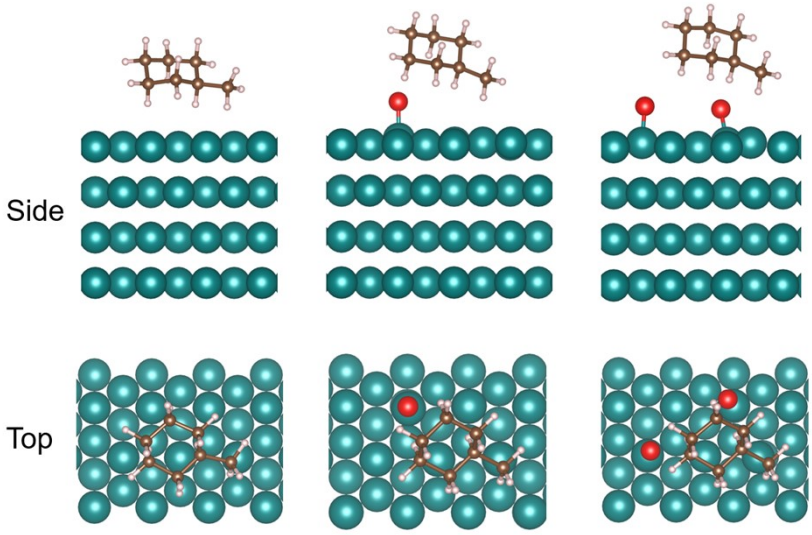

Figure S9. The adsorption behaviors of methylcyclohexane molecule on the Pt(111) surface with zero, one and two O atoms.

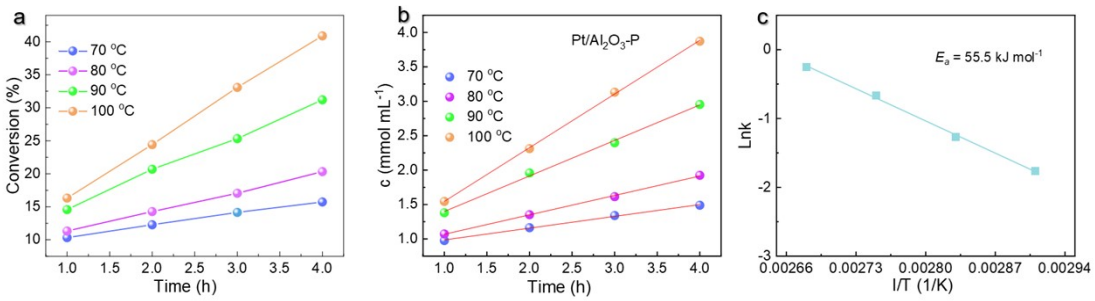

Figure S10. (a) The time course of toluene conversion catalyzed by Pt/Al_2O_3-P. (b) Molar concentration of toluene as a function of reaction time at various temperatures catalyzed by Pt/Al_2O_3-P. (c) ln *k*, derived from conversion rate of toluene, as a function of 1/*T* over the Pt/Al_2O_3-P catalysts. **Reaction conditions:** toluene (14.2 mmol), catalysts (10 mg), 80 °C and 2 MPa H_2.

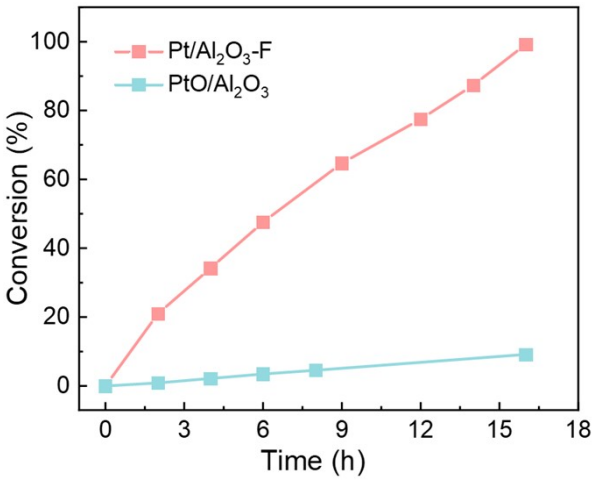

Figure S11. Catalytic activity of PtO/Al_2O_3 for toluene hydrogenation. **Reaction conditions:** toluene (14.2 mmol), catalysts (10 mg), 80 °C and 2 MPa H_2.

Table S1. The ICP-OES results of Pt loading in the Pt/Al_2O_3-F and Pt/Al_2O_3-H catalysts.

Entry	Catalysts	Pt loading (wt.%)
1	Pt/Al_2O_3-F	1.03
2	Pt/Al_2O_3-H	1.01

Table S2. Summary of the surface Pt^0 and Pt^{2+} fractions of various catalysts obtained from the Pt 4d peaks.

Catalysts	Area				Pt^0 fractions (%)	Pt^{2+} fractions (%)
	$4d_{5/2}$		$4d_{3/2}$			
	Pt^0	Pt^{2+}	Pt^0	Pt^{2+}		
Pt/Al_2O_3-B	1015.7	206.5	595.4	138.4	82.4	17.6
Pt/Al_2O_3-P	645.3	280.0	432.3	187.6	69.7	30.3
Pt/Al_2O_3-H-Air	1000.5	670.3	469.2	314.4	68.1	31.9
Pt/Al_2O_3-F-H_2	1616.5	686.0	1083.1	459.6	70.2	29.8
Pt/Al_2O_3-F	592.3	550.0	394.9	366.7	51.8	48.2
Pt/Al_2O_3-H	736.5	222.8	491.0	148.5	76.8	23.2

Catalysts	Area	Pt^0 fractions (%)	Pt^{2+} fractions (%)
Pt/Al_2O_3-B		82.4	17.6
Pt/Al_2O_3-P		69.7	30.3
Pt/Al_2O_3-H-Air		68.1	31.9
Pt/Al_2O_3-F-H_2		70.2	29.8
Pt/Al_2O_3-F		51.8	48.2

Pt/Al_2O_3-H	76.8	23.2