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Supporting Information

Efficient Alcohols Fuel Oxidation Catalyzed by a Novel Pt/Se Catalyst

Meng Zha^{a,b}, Zong Liu^{a,b}, Quan Wang^a, Guangzhi Hu^{a*} and Ligang Feng^{b*}

^aSchool of Chemical Science and Engineering, School of Energy, Yunnan University, Kunming 650091, China.

Email: guangzhihu@ynu.edu.cn

^bSchool of Chemistry and Chemical Engineering Yangzhou University, Yangzhou, 225002, PR China. Email: ligang.feng@yzu.edu.cn; fenglg11@gmail.com

Experimental method

Materials and chemicals

All the reagents in the experiment were analytical grade and used as received. Selenium dioxide (SeO₂), glucose $(C_6H_{12}O_6)$, hexachloroplatinic acid $(H_2PtCl_6 \cdot 6H_2O)$, ethylene glycol $(C_2H_6O_2)$, L-ascorbic acid were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sulphuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion (5 wt.%) was purchased from Sigma-Aldrich. All solutions were prepared with ultrapure water (Thermo Fisher Scientific (USA) Co., Ltd). The commercial Pt/C catalyst with 20 wt.% Pt loading was purchased from Johnson Matthey Chemicals Ltd with the average particle size of about 3.5 nm.^{1, 2}

(1) Preparation of Se spheres

First, 0.18 g of SeO₂ and 1.5 g of glucose were added into a beaker and dissolved in 15 mL ultrapure water under vigorous magnetic stirring at room temperature to form a homogeneous solution. Then the solution was transferred into the Teflon-lined stainless steel with a volume capacity of 20 mL, sealed and reacted at 200 °C for 6 h. The product was filtered to obtain black precipitate. Finally, the precipitate was washed three times with anhydrous ethanol and ultrapure water, and then dried overnight in vacuum at 60 °C to get the Se catalyst.

(2) Preparation of Pt/Se catalysts

80 mg of Se microspheres obtained above were ultrasonically dispersed in 100 mL ethylene glycol in a flask to form a uniform suspension. A certain amount of H_2PtCl_6 solution (containing 20 mg of Pt) was added to the suspension under stirring. After mixed well, 100 mg of ascorbic acid was added into the above-mentioned solution. The solution was heated to 150 °C in an oil bath to keep the reaction for 3 hours. The final product was obtained by filtration; the precipitate was washed three times with anhydrous ethanol and ultrapure water, and dried overnight in vacuum at 60 °C before use.

Characterizations

The catalysts were characterized by Bruker D8 advance X-ray diffraction (XRD) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurement was carried on an ECSALAB250Xi S3 spectrometer with an Al Kα radiation source. The morphology was examined with an FEI Sirion-200 scanning electron microscope (SEM) and a transmission electron microscope (TEM) operating at 200 kV.

Electrochemical Measurements

All electrochemical measurements were performed using a bio-logic VSP electrochemical workstation (bio-logic Co., France) and a conventional three-electrode system. The working electrode was a catalyst coated glassy carbon electrode (diameter 3 mm, 0.07 cm⁻²). The graphite rods and saturated calomel electrodes (SCE, Hg/Hg₂Cl₂) were used as the counter and reference electrode, the reference electrode was placed close to the working electrode through a double-salt bridge

with a single-tube capillary tip. The potential was carefully checked before and after measurement to ensure the accuracy of the reference electrode. The catalyst ink was a mixture of 4 mg of catalyst, 1 mg of carbon black, 950 μ L of ethanol, and 50 μ L of a 5 wt. % Nafion solution dispersed by ultrasound. Next, 5 μ L of the catalyst ink was pipetted onto a precleaned glass carbon electrode and let the ink dry naturally before use.

Cyclic Voltammetry Measurements:

The electrolyte was firstly bubbled with high purity nitrogen for 15 minutes to remove the dissolved oxygen. The methanol oxidation experiment was conducted in an electrolyte of mixed solution of 0.5 M H₂SO₄ and 1.0 M CH₃OH at a potential range between -0.2 V and 1.0 V vs. SCE at a potential scan rate of 50 mV s⁻¹. The oxidation of ethanol was measured in an acidic solution carried out at room temperature in 0.5 M H₂SO₄ and 1.0 M CH₃CH₂OH solution at a potential range between -0.2 V and 1 V vs. SCE at a potential scan rate of 50 mV s⁻¹. Cyclic voltammograms of the Pt/Se (a) and Pt/C (b) catalysts for methanol and ethanol oxidation were also done at scan rates of 5, 10, 20, 50, 100 mV s⁻¹ and the corresponding peak current density versus the square root of the scan rates was plotted to evaluate the catalytic kinetics. The relationship between the peak current density and the square root of scan rates complies with the following equation: $i_p=2.99 \times 10^5 n(\alpha n')^{1/2}AC_{\infty}D_0^{1/2}v^{1/2}$, where i_p is the peak current density, n is the electron-number for the total reaction, n' is the electron- number transferred in the rate-determining step, α is the electron transfer coefficient of the rate-determining step, A is the electrode surface area, C_{∞} is the bulk concentration of the reactant, D₀ is the diffusion coefficient, v is the potential scan rate. In this paper, the slope of the i_p vs. the square scan rate. In the same electrolyte and the same reaction, the parameters n, C_{∞} and D₀ are constant; Therefore, the slope is decided by $\alpha n'.^3$

CO stripping measurements:

To calculate the electrochemical surface area (ECSA), CO-stripping experiments were carried out. The high purity CO (99.9%) was bubbled to the electrolyte 0.5 M H₂SO₄ for 20 minutes when the potential was controlled at 0 V vs. SEC. Then the nitrogen was bubbled to the electrolyte for 15 min to remove the excess CO dissolved in the electrolyte. The potential range of CO stripping was $-0.2 \sim 1.0$ V vs. SCE at a potential scan rate of 20 mV s⁻¹. The electrochemical active surface areas (ECSA) was estimated by the CO stripping test, assuming that the coulombic charge required for the oxidation of the CO monolayer was 420 µC cm⁻².

Chronoamperometry measurements:

To evaluate the stability of the acidic methanol oxidation catalyst, the chronoamperometry (CA) experiment was carried out in $0.5 \text{ M H}_2\text{SO}_4$ and $1 \text{ M CH}_3\text{OH}$ solutions at 0.6 V vs. SCE for methanol oxidation, and in $0.5 \text{ M H}_2\text{SO}_4$ and $1 \text{ M CH}_3\text{CH}_2\text{OH}$ solution at 0.6 V vs. SCE for ethanol oxidation.

Electrochemical Impedance Measurements:

The electrochemical impedance spectra (EIS) were recorded at the frequency range from 1000 kHz to 30 mHz. The amplitude of the sinusoidal potential signal was 5 mV.

Supporting Figures and Tables



Figure S1. TEM images of the edge of Pt/Se catalysts



Figure S2. The particle size distribution histogram of Pt/Se catalyst.



Figure S3. The high-resolution XPS spectra of (a) Pt/Se catalysts and Pt/C catalyst in the C 1s region.



Figure S4. The High-resolution XPS spectra and of Pt/Se catalysts in the Se 3d region.



Figure S5. Graphical comparison of mass and specific activity of Pt/Se and Pt/C catalysts for methanol oxidation.



Figure S6. Equivalent circuit for EIS analysis. For equivalent circuits, R_S represents uncompensated solution resistance; R_{CT} corresponds to charge transfer resistance generated by alcohol oxidation. R_0 may be related to the contact resistance between catalyst material and glassy carbon electrode. The constant phase element (CPE) is for double layer capacitance and the L from external circuit inductance, usually do not involve the electrochemical process.



Figure S7. Cyclic voltammograms of the Pt/Se (a) and Pt/C (b) catalysts in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ at scan rates of 5, 10, 20, 50, 100 mV s⁻¹ and the corresponding peak current density versus the square root of the scan rates.



Figure S8. Graphical comparison of mass and specific activity of Pt/Se catalysts and Pt/C catalysts for ethanol oxidation.



Figure S9. Cyclic voltammograms of the Pt/Se (a) and Pt/C (b) catalysts in 0.5 M H_2SO_4+1 M CH_3CH_2OH at scan rates of 5, 10, 20, 50, 100 mV s⁻¹ and the corresponding peak current density versus the square root of the scan rates.

Element	Weight %	Atomic %
С	2.26	14.66
Se	78.74	77.8
Pt	19.00	7.54

Table S1. The energy-dispersive X-ray spectroscopy (EDX) composition of Pt/Se catalysts.

ootolysts		$4\mathbf{f}_{7/2}$		4f _{5/2}	Deletive content of D42+/ 0/	
	peak	Binding energy/eV	peak	Binding energy/eV	• Kelative content of Ft-7 %	
Dt/C	Pt ⁰	71.6	Pt ⁰	74.9	10.2	
Pt/C Pt ²⁺	72.8	Pt ²⁺	76.1	19.2		
Dt/Ca actalyzata	Pt ⁰	72.0	Pt ⁰	75.3	46.4	
Pt/Se catalysis	Pt ²⁺	73.2	Pt ²⁺	76.5		

Table S2. Binding energies of Pt $4f_{7/2}$ and $4f_{5/2}$ components for Pt/Se catalysts and Pt/C

Table S3. Electrochemical active surface area (ECSA) estimation from CO stripping voltammetry experiment and peak potential for CO stripping for Pt/Se catalysts and Pt/C catalysts in 0.5 M H_2SO_4 with a scan rate of 20 mV s⁻¹.

Catalysts	ECSA/m ² g _{Pt} ⁻¹	Peak Potential/V
Pt/Se catalysts	67.6	0.52
Pt/C	65.3	0.54

Table S4. Comparisons of activities of various Pt-based catalysts reported in recent years in the 0.5 M H_2SO_4 +1 MCH₃OH solution.

Catalyst	Mass activity/mA mg _{Pt} ⁻¹	reference
Pt-Ag	400	4
PtPdRu	436	5
Pd@mPtAu	415	6
Pt/DSCT hollow spheres	462	7
Pt-MoP/C	680.7	8
Pt-Pd hollow nanoparticles	580	9
Pt-Ni-P nanoparticles	360	10
PtNiP/C catalyst	362	11
TePbPt nanotubes	532	12
Pt@MoS2/NrGO	448	13
Pt/Se	727.5	This work
Pt/C	275.7	This work

Table S5. EIS fitting parameters from equivalent circuits for different catalysts in the $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ solution.

catalysts	R_{S}/Ω	R_{CT}/Ω	R_0/Ω
Pt/Se	8.44	260.5	1.45
Pt/C	7.6	1900	40.5

catalysts	Mass activity/mA mg _{Pt} ⁻¹	Reference
PtSnRu ₂	418	14
Pt _{2.3} Ni/C	638	15
PtRuRh	603.9	16
Pt/TiO2 spheres	250	17
PtCu nanostars	629	18
Pt/C-Cu3P	413.96	19
Pt-NiO nanoparticles	637	20
PtSn sheets	673.6	21
Pt-CoSn	454.6	22
Pt/Se	684.9	This work
Pt/C	245	This work

Table S6. Comparisons of activities of various Pt-based catalysts reported in the 0.5 M H_2SO_4 +1 M CH_3CH_2OH solution.

Table S7. EIS fitting parameters from equivalent circuits for different catalysts in the $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{CH}_2\text{OH}$ solution.

Catalysts	R_{s}/Ω	R_{CT}/Ω	R_0/Ω
Pt/Se	7.59	754	20.33
Pt/C	8.33	1732	36.4

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