Electronic Supplementary Materials

In situ Manipulation of d-band Center in Metals for Catalytic Activity in CO Oxidation

Kyung Rok Lee,^{‡a} Danim Yun,^{‡a} Dae Sung Park,^b Yang Sik Yun,^a Chyan Kyung Song,^a Younhwa Kim,^a Jungwon Park^a and Jongheop Yi^{*a}

^a. School of Chemical and Biological Engineering, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul, S. Korea. E-mail: jyi@snu.ac.kr

^b. Center for Convergent Chemical Process, Korea Research Institute of Chemical Technology, Daejeon, 34114, S. Korea.

⁺ Electronic Supplementary Information (ESI) available: See DOI: 10.1039/ x0xx00000x

[‡] These authors contributed equally to this work.

S1. Materials and Methods

S1.1 Materials

Pt/C and Au/C catalysts were prepared by incipient wetness impregnation method. The carbon black (Ketjen Black EC 600 JD, Lion Corporation) was used as a support because of its high electric conductivity and surface area. The carbon black was impregnated with the aqueous solution of the platinum (H₂PtCl₆·6H₂O; Sigma Aldrich) and gold (HAuCl₄·xH₂O; Sigma Aldrich) precursors, and the amount of supported metal was controlled to 5 wt%. After drying at 60 °C in the oven, the sample was reduced at 500 °C for 1 h under the stream of 10 % H₂/N₂.

S1.2 Methods

Calculations using COMSOL multiphysics

The temperature distribution of the catalyst bed during current-assisted catalysis was calculated using COMSOL Multiphysics 4.3 software. Table S1 lists the used parameters for simulation. Physics-controlled mesh (extra coarse mesh) was used along with joule heating and heat transfer for a porous media physics module. The volumes for the entire system (Pt/C) and the platinum metal were $230 \times 230 \times 230$ nm³ and $(4/3) \times \pi \times 10^3$ nm³, respectively. The platinum metals were arrayed in a $4 \times 4 \times 4$ pattern in the carbon black support and the distance between the nanoparticles was controlled to 50 nm. In the boundary condition, not only the electric potential, but also the flow of gases through the z direction was considered. The applied voltage through the catalyst bed was 1.31×10^{-5} V.

Table S1. Parameters used in the simulation of a current-assisted catalytic system

Parameter	Carbon black	Platinum
Thermal conductivity $[W \cdot m^{-1} \cdot K^{-1})]$	150	71.6
Electrical conductivity $[S \cdot m^{-1}]$	1000	9.43×10^{6}
Heat capacity [J·kg ⁻¹ ·K ⁻¹)]	900	125.6
Density $[kg \cdot m^3]$	180	21.45×10^{3}

High Resolution Transmission Electron Microscope (HR-TEM)

The size of the metal particles was observed using a high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100) with an acceleration voltage of 200 kV.

X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were collected by Rigaku d-MAX2500-PC powder X-ray diffractometer with Cu K α radiation (1.5406 Å), operated at 50 kV and 100 mA.

N2 adsorption-desorption

The N_2 adsorption-desorption isotherms were obtained at -196 °C using an ASAP-2010 (Micromeritics). The total surface area of the Metal/C samples was calculated by the Brunauer-Emmett-Teller (BET) method.

in situ X-ray absorption spectroscopy (in situ XAS)

In situ X-ray absorption near edge structure (*in situ* XANES) analysis for the L_2 and L_3 edges in the platinum and gold was performed at the Pohang accelerator laboratory (PAL) 8C beamline in the 3.0 GeV storage ring. All *in situ* XANES data were calibrated for Au and Pt foil under room temperature. A Si(111) double crystal monochromator (DCM) tuned and detuned the beam energy to exclude the harmonics. An ionic chamber was used to detect the I_o and I_t of the samples. A copper line connected the samples to a power supply that provided electric current through the samples during the measurement. The collected XANES data were normalized by Athena software.

CO chemisorbed temperature-programmed oxidation (TPO)

CO-temperature programmed oxidation (TPO) results were obtained using an on-line mass spectrometer (QGA, HIDEN ANALYTICAL). A 0.1 g sample of catalyst was loaded and the sample was pretreated at 100 °C for 30 min with 100 ml/min of He. The sample was treated for 15 min with 125 ml/min of 10% CO/He for CO chemisorption, then the physisorbed CO was purged with 100 ml/min of He for 7 minute. Then, 10% O_2 /He was introduced at a flow rate of 20 ml/min, and the O_2 that reacted with the chemisorbed CO on the Pt was monitored via MS signal (m/z=44, CO₂). During this measurement, the temperature of the reactor was kept at 100 °C for 7 min and then the sample was heated up to 400 °C at a ramping rate of 30 °C/min.

Catalytic activity test

The CO oxidation was performed in a flow-type quartz reactor under atmospheric pressure at various temperatures. A 0.1 g sample of catalyst was used and the sample was pretreated at 500 $^{\circ}$ C for 1 h (5 $^{\circ}$ C/min) in a flow of 10% H₂/N₂ (40 mL·min⁻¹). The temperature was controlled to reaction temperature and stabilized for 30 min. The feed stream consisted of CO, O₂, N₂ and He with a volumetric ratio of 1:1:2:96, at a total flow rate of 100 ml/min. The catalyst bed was placed between the carbon electrode (GDL 39BC, SGL carbon), which was connected to the power supply by copper wire. Rectangular shape of quartz reactor was used to induce uniform and planar electric field through the catalyst bed. Catalytic bed and carton electrode are fixed by quartz wool during the activity test. Schematic explanation for our catalytic reaction system is presented in Fig. S1. The catalytic activity with electric field was recorded at 170 °C and 300

°C on each Pt/C and Au/C. The kinetic studies was conducted at 150 °C and 240 °C on each Pt/C and Au/C to keep the conversion rate less than 10 %. During the kinetic study, partial pressure of the other reactant gas was fixed at 7.6 mmHg. The products were analyzed using an on-line gas chromatograph (Younglin, ACME 6000 model) equipped a Shincarbon (RESTEK, ST 100/120) column and a thermal conductivity detector. The conversion of CO was calculated as follows:

 $CO \text{ conversion (\%)} = \frac{\text{mole of CO reacted}}{\text{mole of CO fed}} \times 100$

Computational methods

Periodic DFT calculations were conducted by using a Vienna ab initio simulation package (VASP) software. Generalized gradient-approximation and Perdew-Burke-Ernzerhof (PBE) exchanged-correlation functional was used with a projector-augmented wave (PAW) method to describe the core electrons. An energy cutoff of 400 eV and a 4 x 4 x 1 Monkhorst-Pack k-point mesh was set in this calculation. Pt(111) and Au(111) surface was modeled with a five-layer metal slab, and inner two layers were fixed after the geometry optimization of a super cell. The vacuum gaps between each metal slab in the z direction were three times longer than the thickness of the five-layer of metal, which was sufficient to ignore the influence the electric field from the upper periodic super cell. The adsorption energy of the gas molecule on each metal surface, ΔG_{ads} , was investigated with following formulation:

$\Delta G_{ads} = G_{ads - surface} - G_{adsorbate} - G_{surface}$

Here, Gads-surface, Gadsorbate, and Gsurface are the total energy of each metal surface with adsorption, gas molecule in a vacuum and clean metal surface.

S1.3 Magnitude of electric field at catalytic bed

To calculated the magnitude of electric field, the potential difference at each reactor system component is necessary because the uniform and planar electric field passed into the catalytic bed and the magnitude of electric field is acquired by diving the potential difference by the distance between the electrode. For our catalytic reaction system, copper wire, carbon electrode and catalytic bed are arranged in a chain and electric current flows through the reactor components sequentially. It means that our reaction system is able to be regard as a series circuit and the components act like a resistance. Thus, total voltage is the sum of the voltage drop occurred at each resistance and each voltage drop is calculated by using Ohm's law. The resistance (R) of each part is defined as:

$$R = \rho \frac{l}{A}$$

where ρ is specific electrical resistance of the material, 1 is length and A is cross-section area of component, which are presented in Table S2. With the equation and the physical properties of each part, resistance, potential difference and magnitude of electric field are able to be calculated and are exhibited in Table S2.

	copper wire	carbon electrode	catalytic bed
specific electrical resistance [Ω•m]	1.72×10 ^{-8a}	2.40×10 ^{-3b}	3.90×10 ^{-2c}
length [m]	0.4	5.00×10 ⁻⁵	0.01
cross-section area [m ²]	7.85×10 ⁻⁷	1.40×10^{-4}	1.00×10 ⁻⁴
resistance $[\Omega]$	8.78×10 ⁻³	8.57×10^{-4}	3.9
potential difference [V]	8.98×10 ⁻⁴	8.77×10 ⁻⁵	3.99×10^{-1}
electric field [V•m ⁻¹]	2.25×10 ⁻³	1.75	39.9

Table S2. Physical properties and calculated rsults of circuit component¹



Fig. S1. Schematic illustration of current-assisted catalytic system to apply the electric potential into the Carbon supported metal catalysts.



Fig. S2. The Joule heating effect on the current-assisted catalytic system with a low level of applied voltage.



Fig. S3. (a) Model structure (o: Pt nanoparticles) and (b) temperature distribution of Pt/C during current-assisted catalysis calculated by COMSOL multiphysics



Fig. S4. (a) TEM image, (b) XRD pattern, and (c) nitrogen adsorption-desorption isotherm of a fresh Pt/C catalyst



Fig. S5. (a) TEM image, (b) XRD pattern, and (c) nitrogen adsorption-desorption isotherm of a fresh Au/C catalyst



Fig. S6. Adsorption behavior of CO on Au/C with and without applied voltage. CO_2 signal was monitored by *in situ* TPO-MS after pre-adsorbing of CO on Au/C



Fig. S7. (a) XRD patterns and (b) TEM images and distribution of nanoparticle of Pt/C after the reaction test.



Fig. S8. (a) XRD patterns and (b) TEM images and distribution of nanoparticle of Au/C after the reaction test.



Fig. S9. Catalytic activity on the platinum and gold catalyst with and without applied voltage at $170 \text{ }^{\circ}\text{C}$ (Pt) and $300 \text{ }^{\circ}\text{C}$ (Au), respectively.





high θ_{co}

Fig. S10. Schematic explanation for mechanism of CO oxidation on Pt/C with different coverage of CO



Fig. S11. Schematic illustration of CO oxidation on Au with different electric condition



Fig. S12. Adsorption energy of (a) CO and (b) O_2 on the Pt metal slab and (c) CO and (b) O_2 on the Au metal slab. A diamond and triangle symbol indicate the value of CO and O_2 , and filled and empty symbol means the value of Pt and gold, respectively.

S2. Reference

1 aCRC Handbook of Chemistry and Physics, 64th ed; bSigracet 39 BC, https://www.fuelcellstore.com/sigracet-39bc, Jan 2021; cKetjen black, https://www.lionspecialty-chem.co.jp/en/product/carbon/carbon01.htm, Jan 2021