

Surface Conductivity Measurement of Catalyst Materials by EUPS and Its Correlation to Catalyst Performance

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ABSTRACT

Commercial three way catalysts (TWC) are designed to eliminate HC, CO and NO_x pollutants emitted from gasoline powered internal combustion engines. TWC have been optimized over many years to meet ever more stringent emission regulations. It has long been speculated that surface electrical conductivity may be a key parameter in controlling catalytic activity, however until now it has not been possible to reliably measure this physical parameter on a catalytic surface.

In this study, the surface electrical conductivity of catalyst powders, such as Rh/CeO_{1-x}-Zr_xO₂, Rh/ZrO₂ and Rh/Al₂O₃, were measured by EUPS (Extreme Ultraviolet excited Photoelectron Spectroscopy). Then the measured electrical conductivity was compared with catalyst performance from CO-NO and water gas shift reactions which are important for controlling automobile exhaust emissions from gasoline vehicles. Good correlation was observed between the surface electrical conductivity and catalytic light-off performance for both reactions, thus linking the contribution of the surface electrical conductivity to catalytic activity.

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INTRODUCTION

Automobile exhaust catalysts are required to reduce pollutant emissions such as CO, HC (hydrocarbons) and NO_x from gasoline vehicles. The emission control product which accomplishes this objective is known as a Three Way Catalyst (TWC), and is composed of precious metals, aluminum oxide, and ceria-zirconia solid solution. Because of increasingly stringent emission control regulations, further catalyst development is desired and is the subject of ongoing research. To achieve the better performance required by rigorous new regulations, detailed catalyst characterization is essential, especially with respect to understanding the surface of catalyst materials. For reactions that proceed on a catalyst surface, the rate controlling step may be oxygen and/or electron mobility which can be considered as aspects of surface electrical conductivity. It has long been speculated that surface electrical conductivity may be a key parameter in controlling catalytic activity, however until now it has not been possible to reliably measure this physical parameter on a catalytic surface. Although there are some well know methods to measure electrical conductivity of materials, it is often performed on single crystal surfaces or flat surfaces that have been pre-sintered at high temperature (>1300°C), and in many case these surfaces are significantly different from the actual surface structure of active catalysts [1,2,3].

In this study, the surface electrical conductivity of catalyst powder materials such as Rh/CeO_{1-x}-Zr_xO₂ (referred to hereafter as CZ), Rh/ZrO₂, and Rh/Al₂O₃ was measured by EUPS (Extreme Ultraviolet excited Photoelectron Spectroscopy) developed at the *National Institute of Advanced Industrial Science and Technology* (Figure 1). EUPS is a novel photoelectron spectroscopy, in which a sample is excited with a 4.86nm (255 eV) 3-ns pulse of EUV (Extreme Ultra Violet) light emitted from a laser-produced plasma and a photoelectron spectrum is analyzed with a time of flight (TOF) analyzer [4,5,6,7].

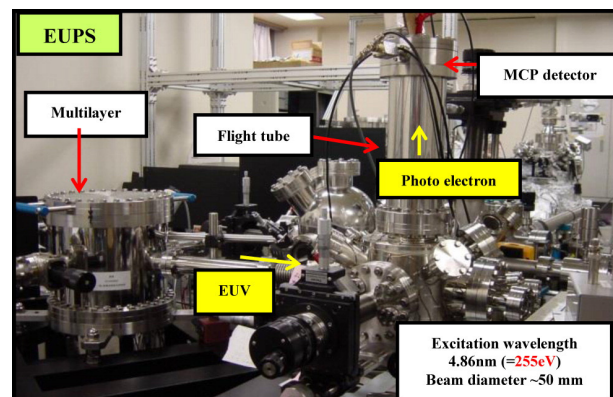


Figure 1. EUPS is the photoelectron spectroscopy system in which 3ns duration 4.86nm EUV light irradiate a sample and the emitted electron spectrum is analyzed by the TOF method.

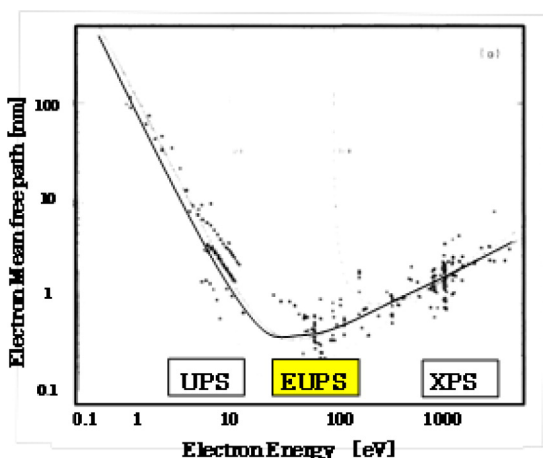


Figure 2. Escape depth of electrons is the minimum at 50 to 100 eV kinetic energy.

Figure 2 shows the relationship between emitted electron kinetic energy and electron mean free path in solids [8]. All materials have similar electron escape depth. Electrons detected by EUPS have the energy of several tens of eV where escape depth is the minimum of one mono-atomic-layer. Therefore, information on electronic states of only the topmost atoms of a sample is obtained by EUPS. The surface electrical conductivity of each catalyst is evaluated by the discharge time constant measured by the EUPS method. To investigate the correlation between catalyst reaction activity and surface electrical conductivity, CO-NO and water gas shift (CO-H₂O) reactions were studied.

EXPERIMENTAL

Measurement of EUPS Method

Because EUPS detects only the topmost atoms, it can detect charging shift in a film as thin as a few nm. Because EUPS uses a pulse source to excite electrons, the discharge time constant can be observed by stopping EUV excitation. By changing repetition rate of the pulse, time averaged excitation power and magnitude of charging shift can be easily varied. Owing to these properties, surface electrical conductivity of catalysts can be easily evaluated by using EUPS.

The catalyst film is charged by E_0 after each EUV pulse excitation. Multiple pulses lead to charge accumulation. However, accumulated charge is discharged with time constant τ and yields a saturated charge shift E as shown by eq. (1).

$$E = E_0(1 - \exp(-\frac{\Delta T}{\tau})) \quad (1)$$

Where,

E = saturated charge shift [eV]

E_0 = charge after each shot [eV]

ΔT = interval of pulses [sec]

τ = time constant of discharge [sec]

The discharge time constant (τ) is given by the product of the capacitance (C') and resistance (R). Charging shift E is larger for a thicker film, however, time constant, $\tau = C'R$, does not depend on the mechanical structure of samples but is determined only by the material constants of permittivity (ϵ) and electrical resistivity (ρ) as shown in eqs. (2) to (4).

$$C' = \epsilon \cdot A/d \quad (2)$$

$$R = \rho \cdot d/A \quad (3)$$

$$\tau = C'R = \epsilon\rho \quad (4)$$

Where,

C' = capacitance [F = CV⁻¹]

ϵ = permittivity [F/m = CV⁻¹m⁻¹]

A = surface area [m²]

d = thickness [m]

R = resistance [Ω]

ρ = electrical resistivity [Ω m]

Although electrical resistivity changes several orders of magnitude depending on material and temperature, dependence of permittivity on materials is relatively small and temperature change is negligibly small. Therefore, by knowing the discharge time constant electrical resistivity (ρ) can be estimated. The inverse of resistivity is the conductivity (σ).

$$\sigma = 1/\rho \quad (5)$$

When τ was longer than several seconds, it was estimated directly from the decay constant of the charging shift by stopping EUV excitation. When τ was shorter, it was estimated from the saturated charging shift E .

Catalyst Preparation

The CeO_{1-x}-Zr_xO₂ (CZ) solid solution used in the study had a CeO₂-Zr_xO₂ mixing ratio 3:7 weight %. Rh supported catalysts were prepared by the conventional incipient impregnation method from CZ, ZrO₂, and Al₂O₃ using an aqueous solution of Rh(NO₃)₃ as the Rh precursor. The loading of Rh in these samples was controlled to 1wt%. All catalysts were calcined at 1000°C in air for 5h prior to evaluation.