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Practical chemical analysis of Pt and Pd based heterogeneous catalysts with hard X-ray photoelectron spectroscopy

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ABSTRACT

Interfacial properties including configuration, porosity, chemical states, and atomic diffusion greatly affect the performance of supported heterogeneous catalysts. Hard X-ray photoelectron spectroscopy (HAXPES) can be used to analyze the interfaces of heterogeneous catalysts because of its large information depth of more than 20 nm. We use HAXPES to examine Pt-doped CeO_2 and related thin film catalysts evaporated on Si, carbon, and carbon nanotube substrates, because Pt-doped CeO_2 has great potential as a noble metal-based heterogeneous catalyst for fuel cells. The HAXPES measurements clarify that the dopant material, substrate material, and surface pretreatment of substrate are important parameters that affect the interfacial properties of Pt-doped CeO_2 and related thin film catalysts. Another advantage of HAXPES measurement of heterogeneous catalysts is that it can be used for chemical analysis of trace elements by detecting photoelectrons from deep core levels, which have large photoionization cross-sections in the hard X-ray region. We use HAXPES for chemical analysis of trace elements in Pd nanoparticle catalysts immobilized on sulfur-terminated substrates and Pt_3Ni nanoparticle catalysts enveloped by dendrimer molecules.

1. Introduction

The structures and properties of supported metal catalysts have found attracted great interest in heterogeneous catalysis for many years. In particular, noble metal catalysts dispersed on oxide substrates have been widely investigated. For example, three-way catalysts (TWCs) for automobile exhaust emission control are composed of catalytically active species such as Pt, Pd, and Rh, a CeO_2 promoter, and an Al_2O_3 support [1]. CeO_2 is an oxygen storage material that widens the operating window (the range of air/fuel ratio around stoichiometry where CO, HC, and NO_x conversion efficiency is satisfactory) by adsorption and desorption of oxygen. TWCs were first developed in the late 1970s, and were used industrially from the beginning of the 1990s. Analysis with X-ray photoelectron spectroscopy (XPS or XPES) has made an important contribution to the promotion of industrial TWCs [1]. This contribution is evidenced by the fact that the number of papers on XPES analysis of car exhaust catalysts has increased rapidly since 1990: the number of papers published during 1990–2010 was more than tenfold that during 1969–1989 [2].

Photoelectron spectroscopies and microscopies play very important roles in the study of heterogeneous catalysts [3]. An example of the historic research on the catalytic reaction on a noble metal catalyst is Gerhard Ertl's Nobel-Prize-winning work, where he clearly visualized the dynamic chemical reaction of CO oxidation on a Pt(1 1 0) catalyst using photoemission electron microscopy (PEEM) [4,5]. He revealed the mechanism of a complicated chemical reaction where bistable states (CO- and O-rich states) were spatially partitioned and grew in an ordered fashion because of cooperative reactions of adsorption, surface diffusion, and surface phase transition. This is a very successful example of using a surface-sensitive photoemission technique to analyze a heterogeneous catalytic reaction on a well-defined flat surface. However, almost all practical heterogeneous catalysts like TWCs of automobiles do not have a well-defined flat surface; porous and powder catalysts are often used practically. Generally, the morphology of catalysts and supporting materials affects catalytic activity. If one measures the electron spectra of catalysts with a surface-sensitive photoelectron spectroscopy (PES), such as that with ultraviolet light or soft X-rays (SXPES), one observes the extremely limited surface that faces the electron spectrometer. In the case of porous catalysts where reactions occur at active surface sites inside the pores, the high surface-sensitivity of PES does not allow the mechanism of catalytic reactions inside the pores to be investigated. However, PES excited with hard X-rays, commonly known as hard

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X-ray photoelectron spectroscopy (HAXPES), has a large information depth of tens of nanometers, which provides unprecedented suitability to investigate porous catalysts. For nanoporous catalysts with a high surface/bulk atomic ratio, the acquired HAXPES signals contain a substantial amount of surface-based information.

The aforementioned fundamental research using PEEM determined factors such as surface crystal structure, partial pressure of gas, sample temperature and surface atom transport that govern the performance of catalysts. Other important factors of practical heterogeneous catalysts included the layer structure and the atom transport between surface and bulk layers of a catalyst. For example, multilayered TWCs [6] were developed in the early 1990s to meet new emission regulations for lower-emission vehicles. These TWCs are composed of layers that are an optimum combination of noble metal catalysts (Pt, Rh, and Pd) and ceria-based mixed oxide promoters (CeO_2-ZrO_2 and CeO_2-ZrO_2-Al_2O_3). The oxygen storage and release capacity of the promoters is used to chemically stabilize the air/fuel ratio in the exhaust to allow automotive pollution control [7], which is based on the oxygen transport between the surface and bulk of the ceria-based mixed oxide. Generally, in catalysts supported on thin films, e.g., carbon or a silicon wafer, the catalyst–support interaction plays a crucial role in the morphology and inhomogeneity of the catalyst. Therefore, it is important to study the catalyst–support interfacial region to understand catalyst properties. In this case, HAXPES again offers an unprecedented possibility to investigate the catalyst–support interaction because information about interfacial species can be obtained nondestructively.

In this paper, we use HAXPES to study Pt-doped cerium-oxide-based porous catalytic thin films supported by carbon nanotubes (CNTs), carbon thin films and silicon. Pt-CeO_2 catalysts synthesized by magnetron sputtering were deposited as thin films on CNTs [8–10] with a Pt concentration of approximately 4–10 at% relative to the total amount of Ce and O atoms. These catalysts are very active for hydrogen splitting in proton exchange membrane fuel cell (PEMFC) anodes. Our HAXPES studies clarify that the Pt-CeO_2 film catalysts contain entirely ionized Pt in CeO_2, and the ionized states depend on the substrate. Chemical analysis of the overall catalyst layer with HAXPES should aid development of highly functional catalysts because the presence of cationic noble metals stabilized in oxides can increase catalytic activity [11].

Another advantage of using HAXPES to analyze practical heterogeneous catalysts on substrates is its ability to sensitively detect photoelectrons from deep core levels. It is well known that trace elements can promote or limit catalytic activity, so chemical analysis of trace elements is very important for the research on practical catalysts. HAXPES has a high sensitivity for detecting elements heavier than aluminum because of the large cross-sections of photoionization of deep core electrons (binding energy > 1.5 keV) excited by hard X-rays. We present HAXPES analysis of Pd-containing catalysts on sulfur-terminated GaAs or Au substrates as well as that of a small amount of Pt_3Ti nanocluster catalysts embedded in dendrimers from the viewpoint of chemical analysis of catalytic trace elements.

HAXPES can examine the morphology, layer structure, transport of chemical groups in the depth direction, and trace amounts of catalysts or additives, so it is a useful technique to study practical catalysts. It should be noted that a refined approach combining different information-depths using HAXPES and SXPES has also been developed [12], which we do not discuss in this report.

2. HAXPES measurements

HAXPES measurements were performed ex situ at the undulator beamline BL15XU at the synchrotron radiation facility SPring-8. X-ray energy was tuned to 5.96 keV. X-rays were monochromatized by a Si 333 channel-cut crystal and the energy width of X-rays was <60 meV. Electron energy was analyzed using a VG Scienta R4000. The total energy resolution was estimated to be 250 meV by observing the Fermi edge of an Au reference samples. The binding energy was also calibrated by the Fermi edge of an Au reference sample. The brilliant X-ray from the undulator source could efficiently detect small amounts of catalysts, but the X-ray sometimes damaged the porous oxide or organic catalysts. Minimizing X-ray exposure time at a fixed point on the sample was important to prevent damage of easily decomposable samples.

3. Results and discussion

3.1. HAXPES interface analysis of a thin film of Pt doped CeO_2 and related catalysts supported on flat Si, carbon films and CNTs

The proliferation of electronic devices requires rapid development of suitable energy storage, despite all efforts to reduce their power consumption. Therefore, the development of inexpensive power sources with high energy density is necessary to increase the range of usage and functionality of smart devices. Because of the high energy density of chemical carriers, the direct conversion of chemical into electrical energy via fuel cells (FCs) is at the center of electrochemical research and development. Common PEMFC systems use supported nanopowder catalysts exhibiting a complex structure and a large specific area. For mobile microelectronic devices with small power requirements, microfabricated silicon-based FCs (μ-FCs) represent an attractive new type of power source [13–15]. Like other FCs, the catalyst is the key to performance and, therefore, the most critical component of μ-FC. Planar on-chip μ-FCs, therefore, require catalysts prepared by thin-film techniques, which must exhibit a large active surface area similarly to powder catalysts, and which can be easily doped with active additives.

Recently, the properties of Pt-CeO_2 films prepared by magnetron sputtering have been investigated for use in PEMFCs [8–10]. These catalysts possess a porous structure, as shown below, so a large part of the active catalyst surface is buried. The high kinetic energy of escaping electrons, i.e. high inelastic mean free path of photoelectrons, together with the high brilliance of the X-ray source makes this technique particularly suitable for investigating buried species, e.g., those present on the surfaces of pores. The low surface sensitivity of HAXPES also makes it less sensitive to surface contamination by adsorbates appearing as the sample is transported in air.

A cerium oxide layer was deposited by RF magnetron sputtering from a CeO_2 target in argon working gas at a pressure of 0.4 Pa. The discharge power was set to 100 W. The deposition rate of cerium oxide was calibrated by atomic-force microscopy (AFM) using a Veeco di MultiMode V microscope in tapping mode and was determined to be 0.2 nm min^{-1}. In the case of doped cerium oxide layers, platinum was co-deposited from a Pt target using a second DC magnetron sputtering system. Pt-Sn-CeO_2 thin films were deposited from a composite target prepared by placing pieces of Pt and Sn wires on the ceria target surface in the radial direction.

The CeO_2 based catalysts were grown on silicon substrates covered by oxide layers of different thicknesses and/or on Si wafers coated with a thin film of carbon or CNTs. Si(1 0 0) wafers covered by native oxide layers were used as reference substrates. Thicker silicon oxide overlayers were grown on the Si wafer surface by annealing at 1150 °C for 50 min in air. The thickness of the oxide overlayers was estimated to be $\sim$100 nm based on cross-sectional scanning electron microscopy (SEM) analysis. Carbon layers were deposited by DC magnetron sputtering in a commercial modular high-vacuum coating device (MED 020, Bal-Tec) from a graphite target in argon working gas at pressure of 0.8 Pa. The rate of carbon