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Secondary ion mass spectrometry (SIMS) with Bi_3^+ primary ions as a sensitive probe of surface structures of heterogeneous catalysts

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ABSTRACT

We prepared mesoporous Al_2O_3- or SiO_2-supported Fe-oxide nanoparticles and their geometric and chemical properties were studied. For Fe-oxide/SiO_2, transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns clearly show structure of Fe-oxide with particle sizes of 7–15 nm. However, TEM and XRD did not show clear evidence for the structure of Fe-oxide on Al_2O_3, even though a higher dispersity of Fe-oxide on Al_2O_3 was suggested by elemental mapping techniques. Catalytic activity of Al_2O_3-supported Fe-oxide was much higher than that of the SiO_2-based catalyst for CO oxidation and NO reduction by CO, implying a higher effective surface area of Fe-oxide on Al_2O_3, also in good agreement with Fe-oxide being more highly dispersed on Al_2O_3. SIMS shed more light on the catalyst structure. The Fe^+/Al^+ ratio from Fe-oxide/Al_2O_3 was much higher than the Fe^+/Si^+ ratio from Fe-oxide/SiO_2, in line with our observations from TEM and catalytic activity that Fe-oxide is more highly dispersed on Al_2O_3 than on SiO_2. Moreover, not only Al^+ and Fe^+ but also mixed cluster ions of Fe^+ and Al^+ such as $FeAlO^+$, $Al_2FeOH_2^+$ and $Al_2FeO_3^+$ were observed from the surface of Fe-oxide on Al_2O_3. The presence of these ions comments on chemical bond formation between Fe-oxide and Al_2O_3 at the interface of nanostructured overlayers and substrates. The Fe-oxide/SiO_2 surface produced much less pronounced SIMS emission of $FeSiO^+$ compared to the Fe-oxide/Al_2O_3 surface, suggesting lower dispersion and much larger size of the Fe-oxide particles on SiO_2. Detailed analyses of SIMS spectra can provide deep insight into complex nanostructures.

1. Introduction

Heterogeneous catalysis is of importance in a broad range of applications from environmental purification to alternative energies [1–12]. Toxic and harmful molecules in the atmosphere such as carbon monoxide (CO), nitrogen monoxide (NO) and volatile organic compounds can be catalytically oxidized into non-harmful molecules [4,6,8]. Production of various chemicals relies on heterogeneous catalysis [3]. Conversion of carbon dioxide (CO_2), regarded as responsible for global climate change, to syngas and other value-added products using either thermal chemistry or electrochemistry is also closely related to heterogeneous catalysis [9–12]. Various reactions in fuel cell systems such as oxygen reduction are based on heterogeneous catalysis [5].

Heterogeneously catalyzed reactions mostly take place on the surface of catalytically active solid materials. In order to maximize the effective catalytically active surface area of a given material, catalysts are used in the form of very small nanoparticles dispersed on high-surface-area materials such as Al_2O_3, SiO_2 and porous carbons. Decreasing the catalyst particle size sometimes shows unexpected particle-size dependence in catalytic activity [4,6,13–15].

Choosing proper supporting material for catalytically active nanoparticles not only affects their stability, but also their catalytic activity. Interactions between catalytically active nanoparticles and substrate are highly important in heterogeneous catalysis [16,17]. Strong interactions between catalytically active nanoparticles and substrate can be useful in stabilizing small nanoparticles, since less interaction between nanoparticles and substrate often leads to facile agglomeration of nanoparticles, reducing the surface area

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of the catalytically active portion. In cases such as Au nanoparticles and clusters supported by MgO or TiO_2, substrate-to-metal charge transfer can be a crucial factor for enhancing catalytic activity [18,19].

Recently, we have shown that secondary ion mass spectroscopy (SIMS) from surfaces consisting of Au nanoparticles on SiO_2 using Bi_3^+ as the primary ion can provide direct information regarding the nature of the interaction between Si and Au; when Au nanoparticles only physically attach to the surface, SIMS spectra show emission of pure Au clusters with a well-known even-odd pattern [20]. On the other hand, Au-silicide formation results in the emission of mixed clusters of Au and Si. These results show that SIMS can be used to shed light on the nature of nanoparticle-substrate interactions, which can hardly be studied by any other method [21,22]. X-ray photoemission spectroscopy (XPS) is one possible method for studying this interaction, since core level shifts of the supported nanoparticles can be sensitive to nanoparticle-substrate charge transfer [23,24]. However, particle size and shape can also significantly influence core level shift due to both initial and final state effects, often making interpretation of the core level shift difficult [25–27]. Extended X-ray absorption fine structure (EXAFS) is helpful for shedding light on the local coordination of an atom, though with only short-range order. Because the nanoparticle-substrate interface is not an abundant portion of a sample in terms of the total number of atoms present, analyses using EXAFS can be challenging [28]. The degree of nanoparticle-substrate interaction on various substrates can be qualitatively compared by observing change in nanoparticle size as a function of temperature by electron microscopy. However, microscopic images are generally regarded as representative of the whole catalyst surface. Vigorous statistical studies performed and observed on particles smaller than 1–2 nm using images from various locales of catalysts are also challenging. Also, electron microscopy does not provide evidence on the chemical interaction between nanoparticles and substrates.

Here, we show that SIMS using Bi_3^+ as the primary particle can be used to provide insight into both the structure of catalysts consisting of Fe-oxide nanoparticles and substrates as well as the nature of the nanoparticle-substrate interaction. The differing structures of Fe-oxide/Al_2O_3 and Fe-oxide/SiO_2 will be highlighted based on dissimilarity in the SIMS data of both samples, which reconcile the catalytic activities of both samples for CO oxidation and reduction of NO by CO.

2. Experimental

2.1. Sample preparation

Fe-oxide/Al_2O_3 and Fe-oxide/SiO_2 catalysts were prepared by temperature regulated chemical vapor deposition (TR-CVD), introduced previously [29]. Commercially available mesoporous Al_2O_3 (bead size: 1 mm, mean pore size: 11.6 nm, Sasol) and SiO_2 (particle size: 35–60 mesh (250–500 μm), mean pore size: 15 nm, Sigma Aldrich) were used as the substrate and bis(cyclopentadienyl) iron ($Fe(Cp)_2$, Aldrich) was used as the metal precursor. Oxygen and water vapor already existing in the reactor chamber served as oxidizing agents. 2.5 g of $Fe(Cp)_2$ in a quartz boat (internal size $70 \times 20 \times 8$ mm^3) was placed at the bottom of the chamber and 10 g of mesoporous Al_2O_3 or 5.3 g of SiO_2 in a mesh container was placed above the $Fe(Cp)_2$. The chamber was closed with the lid and sealed with polyimide (PI) tape. First, the temperature of the chamber was increased to 60 °C and maintained for 2 h. During this first step, the originally solid $Fe(Cp)_2$ vaporized, diffused into the porous structure of the substrate, and probably adsorbed on the surface of the substrate. After 2 h, the temperature of chamber was further increased to 200 °C and maintained for 12 h. During this second step, adsorbed $Fe(Cp)_2$ reacted with oxygen or water and formed iron oxide particles. A schematic diagram of the TR-CVD set-up is shown in the Supporting information (Fig. S1).

2.2. Sample characterization

After deposition of Fe-oxide on mesoporous substrate by TR-CVD, the elemental distribution of a cut plane of Fe-oxide /Al_2O_3 and Fe-oxide /SiO_2 was analyzed using a scanning electron microscope (SEM, JEOL, JSM-7100F) equipped with energy dispersive spectroscopy (EDS). To acquire information about the amount of Fe loading on each substrate, inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized. After the as-prepared Fe-oxide /Al_2O_3 and Fe-oxide /SiO_2 samples were annealed at 750 °C for 8 h, the surface area of each sample was determined by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods based on N_2 isotherms (3Flex, Micromerities) and the results were compared with the respective data for bare Al_2O_3 and SiO_2 with and without annealing. For geometric structural information from Fe-oxide /Al_2O_3 and Fe-oxide /SiO_2 annealed at 750 °C, samples were ground and analyzed by high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM, JEOL, JEM ARM 200F) or high-resolution transmission electron microscope (HR-TEM, JEOL, JEM ARM 200F), respectively. XRD spectra of samples were gathered using an X-ray diffractometer (Rigaku, Ultima IV) using Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.54$ Å) with a scanning rate of 4° min^{-1}. Furthermore, Fe-oxide /Al_2O_3 and Fe-oxide/SiO_2 were analyzed by X-ray photoelectron spectroscopy (XPS) for information on chemical states of the elements. Fe-oxide /Al_2O_3 and Fe-oxide /SiO_2 were annealed at 750 °C for 8 h under dry air flow conditions of 30 sccm in the flow system reactor located inside a glove box filled with Ar. These samples were transferred to an ultra-high vacuum (UHV) system by a magnetic transfer system filled with Ar without exposing the samples to the atmosphere. XPS analysis was performed under UHV conditions with a base pressure of 3×10^{-10} torr. The Mg Kα X-ray line (1253.6 eV) was used as the photon source for XPS. XPS spectra were gathered at pass energy of 30 eV by a concentric hemisphere analyzer (CHA, PHOIBOS-HAS 3500, SPECS).

2.3. Catalytic activity test

The catalytic activities of Fe-oxide /Al_2O_3 and Fe-oxide /SiO_2 for CO oxidation and for NO reduction by CO were tested in a flow-type reactor consisting of a quartz tube (internal diameter of 21 mm, length of 300 mm) equipped with a temperature control system. For the CO oxidation test, 10,000 ppm CO gas balanced with dry air was used. 2.0 g of Fe-oxide /Al_2O_3 or 1.3 g of Fe-oxide /SiO_2 were put in a quartz boat (internal size $70 \times 20 \times 8$ mm^3) located at the middle of the reactor; the amount of each catalyst was determined based on the surface area and Fe loading of each sample. Before the catalytic oxidation test, Fe-oxide /Al_2O_3 and Fe-oxide/SiO_2 were pre-annealed at 750 °C under 30 sccm of dry air flow for 8 h. After pre-annealing, the reactor temperature was fixed at 350 °C and CO-containing gas with a CO concentration of 10,000 ppm was injected at a flow rate of 10 sccm. After the total flow of CO was stabilized, the reactor temperature was decreased at a cooling rate of 1 °C/min. During CO oxidation, gas flow was controlled by a mass flow controller (MFC) connected to the reactor. The gasses passed through the reactor were analyzed by an on-line gas chromatographer (GC, Hewlett Packard, HP 6890) equipped with a capillary column (Agilent Technologies, HP-PLOT/Q, 30 m × 0.32 μm) with a methanizer and a flame ionization detector (FID). Catalytic activity for CO oxida-