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Full Length Article

Catalytic activity and stability of nanometic Rh overlayers prepared by pulsed arc-plasma deposition and r.f. magnetron-sputtering

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ABSTRACT

50 μm-thick Fe–Cr–Al metal foils covered by 7 nm-thick Rh overlayers were prepared by pulsed arc-plasma (AP) and r.f. magnetron sputtering technique to compare their catalytic activities. As-prepared metal foil catalysts were wrapped into a honeycomb structure with a density of 900 cells per square inches and the stoichiometric NO–CO–C_3H_6–O_2 reaction was performed at space velocity of 1.2×10^5 h^{-1}. During temperature ramp at 10 °C min^{-1}, honeycomb catalysts showed steep light-off of NO, CO, and C_3H_6 at above 200 °C and their conversions soon reached to almost 100%. Both catalysts exhibited high turnover frequencies close to or more than 50-fold greater compared with those for a reference Rh/ZrO_2 powder-coated cordierite honeycomb prepared using a conventional slurry coating. When the temperature ramping was repeated, however, the catalytic activity was decreased to the different extent depending on the preparation procedure. Significant deactivation occurred only when prepared by sputtering, whereas the sample prepared by AP showed no signs of deactivation. The deactivation is associated with the formation of passivation layers consisting of Fe, Cr, and Al oxides, which covered the surface and decreased the surface concentration of Rh. The Rh overlayer formed by AP was found to be thermally stable because of the strong adhesion to the metal foil surface, compared to the sample prepared by sputtering.

1. Introduction

Three-way catalysts (TWC) are widely used for the exhaust purification system in gasoline-fueled automobiles. In the conventional catalyst formulation, platinum group metals (PGMs) are highly dispersed as nanoparticles in porous washcoat layers coated on monolithic honeycomb substrates, which are consisting of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) ceramics or Fe–Cr–Al metal foils [1–9]. The metal honeycomb enables thinner wall thickness (several 10 μm) and therefore higher cell densities and geometric surface area, greater open frontal areas and lower pressure drops. In addition, the higher thermal conductivity is effective for reducing cold-start emissions. Regardless of the difference of these substrate materials, conventional catalysts were prepared by the same procedure that is via wet processes containing impregnation and slurry coating.

Recently, the authors have reported a dry preparation of metal honeycomb catalysts by pulsed cathodic arc-plasma (AP) deposition [10], which forms the nanometric overlayer of catalytically active metals covering the surface of metal foils. This technique assures strong adhesion of active metals to the substrate and as-prepared metal foil catalysts can easily be converted into a honeycomb shape. More interestingly, one such honeycomb having ca. 3 nm-thick Rh overlayers was found to be very active for simulated TWC reactions under realistic reaction conditions despite their nonporosity and small surface area. The honeycomb exhibited successful light-off of simulated exhausts at a practical gaseous hourly space velocity of 1.2×10^5 h^{-1} due to extremely a high turnover frequency (TOF), the value of which for NO–CO reaction is more than 80-fold greater than that of conventional supported Rh catalysts in a powder form. Because apparent catalytic performance is determined by the mathematical product of TOF and the number of surface Rh atoms, such a high TOF more than compensates a small

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surface area of metal foil catalysts. In other words, the conventional nanoparticle (powder) catalysts require large surface areas and thus large numbers of active sites to achieve required performance, whereas the Rh overlayer catalyst is able to achieve a high performance due to the high TOF in spite of its very small surface area. Therefore, Rh overlayer formed on metal foils has the potential as an alternative design for TWC, which uses less Rh loading than conventional porous powder catalysts.

There is another concern about the preparation procedure of the Rh overlayer catalyst, which may affect the performance and stability. In the present study, the most widely used dry film growth process, r.f. magnetron sputtering, was applied to prepare the Rh overlayer on Fe–Cr–Al metal foils. The catalyst as prepared by AP and sputtering was compared with a focus on their catalytic activity and stability. The catalytic performance was investigated for simulated TWC reaction containing NO, CO, and C_3H_6 under a practical space velocity condition. The structural characterization was performed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Preparation and characterization

The Rh/metal foil samples were prepared by pulsed cathodic AP deposition or r.f. magnetron sputtering. The AP deposition apparatus consists of a vacuum chamber with a turbo-molecular pumping system, an arc discharge source (ARL-300, Ulvac) with a Rh metal cathode (ϕ10 mm, 99.9%, Furuya Metals, Co. Ltd.), and a stage for substrates [9]. A commercially available Fe–Cr–Al metal foil (75 at% Fe, 20 at% Cr, 5 at% Al, Nippon Steel & Sumikin Materials) with a thickness of approximately 50 μm was used as a substrate. When a pressure was below 10^{-3} Pa, a pulsed AP with a period of 0.2 ms and a current amplitude of 2 kA was generated from an Rh metal target with a frequency of 1 Hz and was irradiated onto a metal foil to deposit Rh. The amount of Rh deposition was determined using a quartz crystal microbalance (STM-2, Inficon) and controlled by the numbers of AP pulsing. All deposition processes were carried out at ambient temperature. A reference Rh/metal foil sample was prepared by r.f. magnetron sputtering in a high vacuum system (BC4341, Ulvac) using a standard balanced planar magnetron source operated with a pure Rh target. Before deposition the chamber was pumped to a base pressure below 10^{-3} Pa. Sputtering was performed at ambient temperature in pure Ar at a pressure of 0.3 Pa and a r.f. power of 100 W. In both preparation procedures, the thickness of Rh was adjusted at approximately 7 nm. Flat and corrugated foils (10 mm × 40 mm and 10 mm × 55 mm, respectively) after Rh deposition on both sides were wrapped together into a monolithic honeycomb shape (ϕ8 mm × 10 mm, 900 cells in^{-2}) and fixed in a quartz tube. Fig. 1 shows the photograph of miniature honeycomb thus prepared from flat and corrugated metal foils. A reference 0.4 wt% Rh/ZrO_2 powder-coated cordierite honeycomb was prepared using a slurry coating procedure as described in our previous report [10] (See Supplementary data, Fig. S1). Crystal structure of Rh/metal foils was determined by X-ray diffraction (XRD) using monochromatic Cu Kα radiation (40 kV, 200 mA, RINT-TTR III, Rigaku) in a symmetric 2θ-θ scan mode or an asymmetric detector scan (2θ) mode. The surface texture of Rh/metal foils was observed by a scanning electron microscope (SEM, FEI QUANTA FEG 250 operating at 20 keV). The surface analysis of Rh/metal foils was performed by XPS using a Thermo Scientific K-Alpha spectrometer with monochromated Al Kα radiation (12 keV). The charge-up shift correction of the binding energy was made by using C1 s binding energy at 285 eV.

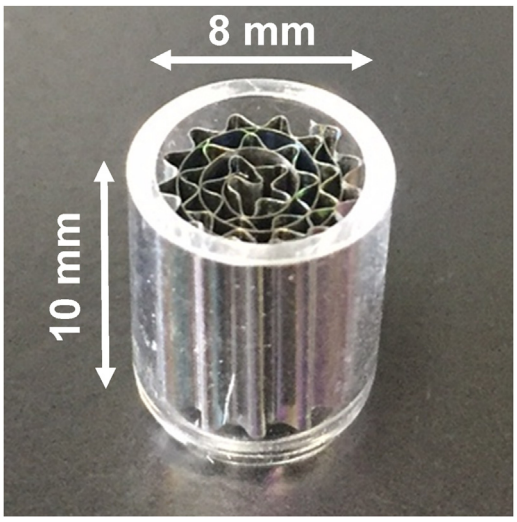

Fig. 1. A photographs of a metal honeycomb consisting of flat and corrugated metal foils.

2.2. Catalytic reactions

Simulated TWC reactions over the honeycomb-shaped catalysts were performed using a Horiba SIGU/MEXA reaction analysis system, which consisted of a gas supply unit, an infrared image furnace with four ellipsoidal reflectors and a gas analysis unit. The catalytic activity was evaluated by heating the catalyst bed from 100 to 500 °C at a rate of 10 °C min^{-1} while supplying the simulated gas mixture (0.05% NO, 0.50% CO, 0.05% C_3H_6, 0.53% O_2, 0.17% H_2, 10% CO_2, 10% H_2O, and N_2 balance, 1.0 L min^{-1}, GHSV = 1.2×10^5 h^{-1}, contact time = 30 ms) at atmospheric pressure. The gas composition corresponds to the stoichiometric air-to-fuel ratio, where all gases can be converted completely into a mixture of CO_2, H_2O and/or N_2. The gas analysis was performed by nondispersive infrared CO/CO_2 detectors, a flame ionization hydrocarbon detector, a chemiluminescence NO_x ($NO + NO_2$) detector and a magnetopneumatic O_2 detector. TOF was calculated from the steady-state NO conversion in the NO—CO—C_3H_6–O_2 reaction below 20% (at 240 °C), which allows a rough approximation for a differential reactor. The number of surface Rh sites for the metal foil samples was calculated using the geometric area of a foil surface, Rh surface coverage and atomic density of the Rh(111) (1.60×10^{19} atom m^{-2}), whereas the TOF value for the powder Rh/ZrO_2 catalyst was determined by CO chemisorption measurement at 50 °C based on 2:1 stoichiometry between chemisorbed CO and surface Rh, which corresponds to the metal dispersion of 17.5% (See Supplementary Data, Fig. S1).

3. Results and discussion

Fig. 2 shows the XRD patterns of the metal foils with and without Rh deposition, which were acquired in a symmetric 2θ-θ scan mode. A bare metal foil shows two peaks (2θ = 44.2 and 64.5°) highlighted by asterisks, which can be assigned to (110) and (200) reflections due to body-centered cubic Fe–Cr–Al alloy. After Rh deposition, two very weak peaks ascribed to the (111) and (200) reflections of face-centered cubic Rh appear. The XRD of Rh overlayer was further studied using a parallel beam geometry and an asymmetric detector scan (2θ) mode at small angles of incidence (ω = 1°) to enhance the reflections from the thin surface layer of the metal foil sample. As shown in Fig. 3, the reflections from the metal foil are less intense, whereas the intensities of three reflections due to Rh are more intense. Notably, the (200) peak is less intense than the (111) peak compared with the relative peak intensities of a pure

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