Synergistic effect of non-precious bimetal catalyst prepared by dual-mode arc-plasma process

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Introduction

Bimetal nanoparticles supported on metal oxides have been extensively studied as catalysts, because structure and reactivity/selectivity of bimetal nanoparticles can be influenced by their chemical compositions. The most conventional procedure for preparing supported bimetal catalysts is wet co-impregnation using aqueous solutions of metal salts. By contrast, dry catalyst preparation using plasmas has attracted considerable attentions. Recently, we have reported that Pd-M (M=Fe, Co, Ni and Cu) bimetal nanoparticles could be formed by synchronizing two pulsed arc-plasmas [1]. The bimetal nanoparticle catalysts supported on CeO₂ exhibited a higher catalytic activity for CO oxidation than those prepared by co-impregnation method.

In the present work, we have applied the dual-mode arc-plasma process for the preparation of non-precious bimetal catalysts, Cr-Cu, to study their catalytic properties. Our interest has also been extended to the structure-catalysis relationship in comparison with each monometal catalysts.

Materials and Methods

Cr-Cu/γ-CeO₂ catalyst was prepared by synchronous pulsed cathodic arc-plasma process. The pulsed arc-plasmas with a period of 0.2 ms and current amplitude of 2 kA were generated from each source with a frequency of 1 Hz. The plasmas generated from each cathode entered into a container, which contained powdered CeO₂ (173 m²/g) under mechanical stirring. The amounts of Cr and Cu loading were controlled by the number of pulses to be around 0.2 wt% each. As-prepared catalysts were thermally aged at 900 °C for 25 h in 10% H₂O/air.

The structure of the catalyst was characterized by TEM/EDX, FT-IR, XRD, XRF, XPS and XAFS (Proposal No. 2012G749, KEK). BET surface area (S BET) was calculated from N₂ adsorption isotherms measured at 77 K. The metal dispersion was determined by the modified pulsed CO technique [1]. Catalytic CO oxidation was carried out in a flow reactor at atmospheric pressure (10 °C/min, 0.1% CO, 1.25% O₂, He balance, W/F=5.0×10⁻⁴ g·min·cm⁻³).

Results and Discussion

Unsupported Cr-Cu nanoparticles were prepared by the pulsed arc-plasma process onto a TEM grid covered with microgrid carbon films. In TEM images, highly dispersed nanoparticles with a narrow size distribution ranging from 5 to 15 nm were observed. The EDX spectra taken from Cr-Cu nanoparticle exhibited Cr and Cu Kα lines, indicating that the single nanoparticle prepared by synchronizing arc-plasmas contained Cr and Cu. The dual-mode arc-plasma with synchronous pulse was found to be useful for the deposition of Cr-Cu bimetal nanoparticles.

Figure 1 shows Cr₂p and Cu₂p XPS spectra of Cr-Cu/γ-CeO₂ before and after thermal ageing at 900 °C. As-prepared catalysts exhibited Cr²⁺ and Cu²⁺. Basically, the arc-plasma process under vacuum yields metallic nanoparticles, but they are partially oxidized when they were exposed to air. After thermal ageing, the fraction of Cu⁺ in mono- and bimetal catalysts was increased to around 80%, probably because Cu should be stabilized as a result of interaction with the surface of CeO₂ upon thermal ageing.

Figure 2 compares light-off curves for CO oxidation over mono- and bimetal catalysts before and after thermal ageing. Although as-deposited Cu and Cr-Cu onto CeO₂ showed slightly lower catalytic activities than Cr₂O₃, they were activated by thermal ageing in spite of the significant loss of surface area due to the sintering of CeO₂ (<10 m²/g). The activation can be explained by the formation of Cu⁰, which plays a key role as an active site for CO oxidation. In addition, thermally aged Cr-Cu/γ-CeO₂ exhibited the higher Cu dispersion as was determined by CO chemisorption at 50 °C. Consequently, thermally aged Cr-Cu/γ-CeO₂ was found to be the most active catalyst for CO oxidation in a series of bimetal catalysts containing 3d transition elements. The high activity of bimetal catalyst is associated with the high Cu metal dispersion and surface concentration.

Significance

Catalytically active Cr-Cu bimetal nanoparticles could be prepared by synchronizing two pulsed arc-plasmas. After the thermal ageing, the bimetal catalyst was found to be the most active catalyst for CO oxidation because of highly dispersed Cr-Cu oxide particles suitable for CO chemisorption.

References