Experimental and computational studies about CO-NO reaction mechanism on rhodium nanoparticle for three way catalyst.

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Abstract: The CO-NO reaction mechanism on the rhodium (Rh) nanoparticle was investigated by using *in-situ* Fourier transform infrared (FT-IR) spectroscopy and theoretical density functional theory（DFT）calculation. From *in-situ* FT-IR measurement, NO did not adsorb on the Rh surface after oxidation treatment, whereas CO adsorbed on the oxidized Rh surface. It was noticed that the adsorption energy on Rh nanoparticle depends on adsorbates and adsorbed sites from DFT. In particular, NO adsorbed strongly at the edge site of Rh nanoparticle and the bond distance between adsorbed NO was longer than that in gas-phase.

Keywords: Rhodium, Automobile exhaust gas catalyst, CO-NO reaction.

1. Introduction

Three way catalyst (TWC) for gasoline-fueled vehicles consists of rare metals, such as platinum (Pt), palladium (Pd), and rhodium (Rh), with inorganic oxides as the support, such as alumina (Al_2O_3), zirconia (ZrO_2), and ceria-zirconia (CeO_2-ZrO_2). The reduction of toxic nitric oxygen (NOx) gas in the automobile exhaust gas is one of the most important reactions for TWC. Especially, Rh plays as the active catalyst for NOx reduction reaction. It is necessary to understand the NOx reduction process in detail due to reduce an amount of rare metals in the TWC. In this study, we focused on the analysis about CO-NO reaction on the Rh surface by using *in-situ* Fourier transform infrared (FT-IR) spectroscopy and theoretical density functional theory (DFT) calculation.

2. Experimental and Computational Details

2-1. Experimental part

Rh single-nano catalyst[1] and Rh-impregnated catalyst were prepared in this study. Support material of both samples was used $Ce_{0.18}Zr_{0.74}Nd_{0.8}O_2$. Rh content was 0.6 wt%. Transmission electron microscope (TEM) was used to determined particle size and configuration of Rh nanoparticle. *In-situ* FT-IR was measured to clarify adsorption characteristics of CO and NO on the surface of Rh nanoparticle. The catalyst sample was prepared in an *in-situ* FT-IR cell that enabled heating with gas flowing for the sample. FT-IR spectra were recorded with a spectral resolution of 4 cm^{-1} on PerkinElmer Frontier. Sample was heated under 100 % He at 673 K for 10 min. After reduction under 1 % H_2/He at 673 K for 10 min., the catalyst was oxidized under 20 % O_2/He at 673 K for 20 min. Observation of surface species at 573 K was carried out after introducing a reaction gas comprising either 1 % CO/He or 700 ppm NO/He at a flow rate of 30 cm^3 min^{-1}.

2-2. Computational part

As Rh nanoparticle, we prepared cubo-octahedron structure consisted of 55 and 201 atoms. The DFT calculations were carried out using the Viena ab-initio simulation package (VASP)[2]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional under the generalized gradient approximation (GGA) was used with projector augmented wave (PAW) method. 1 × 1 × 1 k-point was sampled. A plane wave cut off energy was set to be 400 eV.

3. Results and discussion

3-1. Characterization of Rh nanoparticle

From the TEM image of the samples, about 2 nm Rh nanoparticles dispersed on the support material in both Rh single-nano catalyst and Rh-impregnated catalyst. The size and configuration of Rh nanoparticle in both samples were almost same. Figure 1 shows *in-situ* FT-IR spectra of adsorbed species under CO and NO gas flow. After oxidation pretreatment of Rh single-nano catalyst, adsorption peak about NO was not observed. On the other hand, when CO gas flowed into the sample cell, three adsorption peaks were obtained. In general, adsorption peak at 2062 cm^{-1} is assigned to linear CO species on Rh. Adsorption peak at 2009 and 2078 cm^{-1} are corresponded to the gem-dicarbonyl complex on Rh, Rh^{+}(CO)$_2$[3]. When NO gas flowed again into the sample cell, adsorption peaks of adsorbed CO were disappeared and peak at 1875 cm^{-1} which is assigned to linear NO species on Rh was appeared. In fact, it is indicated that CO adsorbed on the oxidized surface and removed O located on the surface. Consequently, NO could adsorb on the metallic Rh surface.

3-2. Adsorption energy of NO on Rh nanoparticle

The adsorption energy about O, CO and NO on the surface of Rh nanoparticle was calculated. Figure 2 shows the relationship between atomic distance in adsorbed NO and adsorption energy on Rh$_{55}$ nanoparticle. With increasing the adsorption energy, the atomic distance in adsorbed NO elongated, while distance of gas-phase NO is 1.15 Å. The largest adsorption energy of NO was obtained at the edge of Rh nanoparticle. We clearly found the difference of adsorption energy on Rh nanoparticle in different adsorption sites.

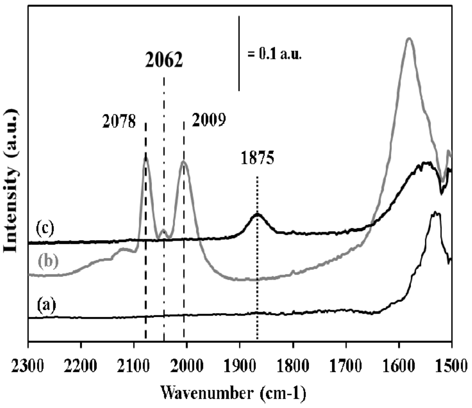

Figure 1. FT-IR spectra of adsorbed species on Rh single-nano catalyst. (a) 700 ppm NO/He for 5 min. after oxidation treatment, (b) 1 % CO/He for 5 min. after 700 ppm NO/He, (c) 700 ppm NO/He for 5min. after 1 % CO/He flow.

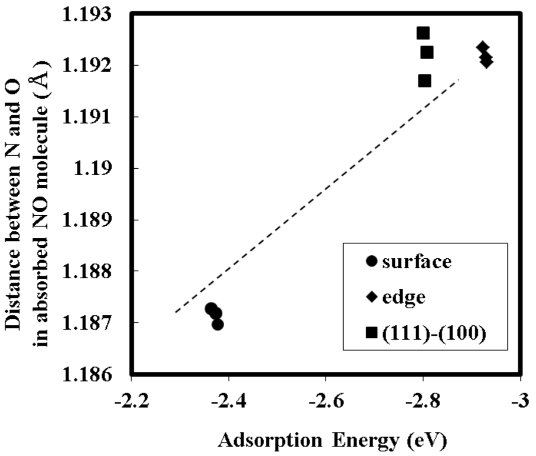

Figure 2. Relationship between bond distance and adsorption energy of NO on Rh$_{55}$ nanoparticle.

4. Conclusions

We investigated the CO-NO reaction mechanism on the surface of Rh nanoparticle by experimental and computational approaches. From *in-situ* FT-IR results, it indicated that changing Rh surface between metallic and oxidized states was dominant of NOx reduction process. On the other hands, from the computational study, when NO adsorbed on the edge site in Rh nanoparticle, the largest adsorption energy was obtained with the longest distance between N and O atoms compared with the other sites. As a result, it is found that the Rh surface condition and adsorption site of nanoparticle affect to the catalytic activity of CO-NO reaction.

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