

Effect of hydrogen on the CO oxidation and NO reduction reactions over a commercial TWC

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Introduction

Three-way catalyst (TWC) has been widely employed to remove three major air pollutants (CO, HC and NO_x) emitted from the gasoline driven engines. The activity of TWC strongly depends on the composition of the reactants contained in the emissions [1-2]. However, the effect of each composition on the TWC activity has not been clearly demonstrated yet. Particularly, although it is well known that hydrogen, commonly existing in the exhaust stream, enhances the TWC activity significantly [1,3,4], the cause of the enhancement effect of H₂ has been hardly reported.

In the present study, the effect of H₂ on the TWC activity over the commercial three-way catalyst has been systematically examined. To identify the role of H₂, the in-situ FTIR analysis has been conducted and then the reaction mechanism has been confirmed for describing the effect of H₂. The kinetic study was also performed to quantify the H₂ effect on the TWC activity from the view of microkinetics.

Materials and Methods

The commercial three-way catalysts including Pd and Pt/Rh/Ce catalysts from GM were specifically examined. The activity of the catalysts has been investigated under the feed condition with and without hydrogen in a packed bed U-type flow reactor immersed in a molten-salt bath to maintain the isothermal reaction condition and 1g of the catalyst power in 20/30 mesh (0.6 – 0.85 mm) size was employed [2]. To investigate the reaction intermediating species adsorbed on the catalyst surface, the FTIR analysis was performed under in-situ conditions using a M2000 spectrometer (MIDAC Corporation).

Results and Discussion

H₂ included in the feed stream enhanced the activity of CO oxidation and NO reduction reactions over both Pd and Pt/Rh/Ce catalysts. H₂ moderates the self-poisoning of CO on the catalyst surface, resulting in improving the oxidation activity of CO. H₂ also reveals the superior NO reducing capability when it is included in the feed gas stream. It indicates that H₂ suppresses the inhibition effect of NO on the CO oxidation reaction [2, 5] by the additional removal of NO. On the other hand, it has been also observed that the enhancing effect of H₂ on the TWC activity tends to be decreased with respect to the catalyst mileage.

To identify the role of H₂ for the TWC activity, the in-situ FTIR analysis under the sequential feed compositions has been conducted over the both catalysts. In the presence of H₂, the

adsorbed OH (3530 cm⁻¹), carboxylate (1593 cm⁻¹) and carbonate (1394 and 1376 cm⁻¹) species have been observed as a reaction intermediate on the catalyst surface during the course of the reaction, particularly over the Pd catalyst, as shown in Figure 1. Based upon this observation, two reaction steps have been deduced for describing the enhancement effect of H₂. One is the reaction of CO and OH (CO·S + 2OH·S → CO₂ + H₂O + 3S). It promotes the oxidation activity of CO at low reaction temperatures. The other is H-assisted NO dissociation reaction between adsorbed NO and H (NO·S + H·S → N·S + OH·S). This reaction step plays an essential role in improving the NO reduction reaction as well as providing OH onto the catalyst surface. Similar results have been also observed over Pt/Rh/Ce catalyst.

Based upon the reaction mechanism confirmed by FTIR analysis, the detailed reaction kinetics has been developed to particularly describe the H₂ enhancement effect. The kinetic model developed in the present study well predicted the experimental data as well as the effect of H₂ over the both catalysts.

Significance

This study suggests that H₂ included in automotive exhaust gas stream mainly contributes to the enhancement of the oxidation reaction of CO with OH and the H-assisted NO dissociation reaction over the commercial TWC.

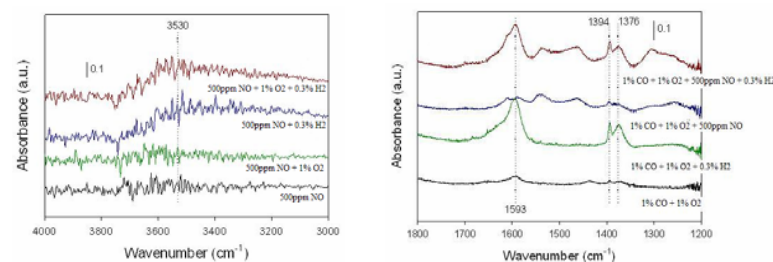


Figure 1. FTIR spectra of OH-stretching and the surface carboxylate and carbonate species vibrational region over Pd catalyst by the in-situ sequential flow at 150°C.

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