An *operando* XAS study on Pt species of Pt/Al_2O_3 during three-way catalytic reaction

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Exhaust gases from gasoline engines in automobiles have been purified by three-way catalysts (TWCs), which convert NO, CO and hydrocarbons (HC) into N_2, CO_2, and H_2O, respectively. TWCs have been studied and used for more than a half century, but direct observation of metal species under model exhaust gas, not only CO-NO, CO-O_2, HC-O_2, is not common. We applied XAS to a model TWC, 1 wt% Pt/Al_2O_3, to analyze redox behavior of Pt species *operando*.

1 wt% Pt/Al_2O_3 was prepared from $Pt(NH_3)_2(NO_2)_2$ aqueous solution and γ-Al_2O_3 by a common impregnation. The powder was calcined at 500 °C for 3 h. A 200 mg of the catalyst was directly pressed into a modified heating XAS cell to secure gas flow path. The catalyst was pretreated under He flow at 400 °C for 30 minutes. After the pretreatment, a model exhaust gas (NO 1000 ppm, CO 1000 ppm, C_3H_6 250 ppm, O_2 912.5–1337.5 ppm and He balance, 100 mL min^{-1}) was introduced into the cell. The concentration of O_2 was changed between 912.5 – 1337.5 ppm during reaction. The stoichiometric condition is achieved when the concentration of O_2 was set to 1125 ppm based on the following chemical equation ($C_3H_6 + 4NO + 4CO + 9/2O_2 \rightarrow 2N_2 + 7CO_2 + 3H_2O$). First, we introduced a lean gas (O_2: 1337.5 ppm) to the cell and changed the oxygen concentration to 912.5 ppm stepwise. The dynamic behavior of Pt species during the reaction was monitored by QXAFS, micro-GC, a NO_x meter and a quadrupole mass spectrometer at a public beamline, BL01B1, SPring-8, Japan.

At the beginning of the reaction under the lean condition, all combustible components were converted into CO_2, NO was converted to N_2 by 70%, and Pt species was slightly oxidized. Next, NO reduction rate abruptly decreased to 60% in about 5 minutes. As the oxygen concentration decreased to reach stoichiometric condition, the NO reduction rate was increased stepwise and reached 100% under the stoichiometric condition as well known. However, average oxidation state of Pt species did not change under lean to stoichiometric condition. When the introduction gas was changed to rich one, the Pt species was gradually reduced to almost metallic state and NO reduction rate decreased. On the other hand, as the oxygen concentration of the reaction gas increased stepwise to the initial one, the conversion rate of the reactants changed in a similar manner when the oxygen concentration decreased, and a part of Pt species was oxidized. In addition, we found interesting phenomena in the NO_x concentration profile. an interesting surface rearrangement behavior, random reduction process and autocatalytic oxidation process of Pt species at the gas switching from reductive to oxidative atmosphere and *vice versa*. The corresponding XAS data indicated successive reduction or oxidation of inner Pt atoms.

We successfully monitored redox behavior of Pt species during three-way catalytic reaction in real time with various probes.

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