Effect of CO_2 on NOx Storage and Reduction (NSR) catalyst studied by spatio-temporal *operando* XAFS

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Improvement of exhaust gas catalyst performance is required because of the strict regulations on automotive exhaust gas emission. NOx is one of the emissions and NOx Storage and Reduction (NSR) catalyst is one of the promising candidates, which realizes low NOx emission. NSR catalyst contains precious metal and NOx storage material, such as alkali or alkali earth metal. NSR catalyst purifies NOx in the exhaust gas by repeating the lean period and the rich period. During the lean period, engine runs with lean burn condition and NOx in the exhaust gas is stored on NOx storage material. During the rich period, engine runs with rich burn condition and stored NOx is reduced to N_2 by reductant gas such as H_2 or CO. NSR catalyst is an integral type reactor and it is predicted that NOx storage and reduction reaction changes from catalyst upstream to downstream. To investigate such integral type reactor and improve catalyst performance, we have developed spatio-temporal operando XAFS technique. In this study, CO_2 effect on NOx dispersion on NSR catalyst was investigated by spatio-temporal operando XAFS.

Operando experiment was conducted at TOYOTA beamline(BL33XU), SPring-8. Rh(0.5 wt%) / Ba (11 wt%) / Al_2O_3 catalyst was put into a capillary tube and the length of the catalyst was about 8 mm. XAFS spectrum of Rh *K*-edge (23.2 keV) was obtained at 4 points A, B, C, and D from catalyst upstream to downstream. The distance between catalyst top and A, B, C and D was 1.0, 3.0, 5.0, and 7.0 mm respectively. Time resolution of XAFS measurement was 0.1 s and beamwidth was ~1 mm. Temperature of the catalyst was sustained at 723 K during the whole experiment. Gas cylinders of 0.07 %NO + 7% O_2/He, 0.07 %NO + 7% O_2 + 10% CO_2/He were used for the lean period without and with CO_2 experiment, respectively. And gas cylinders of 3% H_2/He, and 3% H_2 + 10% CO_2/He were used for the rich period without and with CO_2 experiment, respectively. Before starting XAFS measurement, the lean period continued long enough to saturate NOx storage amount. XAFS spectrum at point A was continuously obtained for 30 s, starting from at the switching from the lean period to the rich period. Continuous XAFS spectrum at the other 3 points was also obtained by repeating the same lean and rich period. Mass spectrometric analysis was performed during the lean period to measure.

By comparing Rh reduction without and with NOx storage, it was clarified that time which needs to reduce Rh oxide to Rh metal increases as the NOx storage amount increases. In both cases of without and with CO_2, stored NOx is equally dispersed from catalyst upstream to downstream. But, the NOx storage amount is almost 1/3 in case of with CO_2, compared to the case of without CO_2. Ba in NSR catalyst is intended to store NOx by forming $Ba(NOx)_2$ (x=2, 3) during lean period. However, CO_2 easily reacts with Ba and forms $BaCO_3$. Since $BaCO_3$ is relatively stable compared to $Ba(NOx)_2$, it is difficult to convert $BaCO_3$ to $Ba(NOx)_2$. This is why NOx storage amount is strongly reduced by the existence of CO_2. Spatially uniform dispersion of NOx from catalyst upstream to downstream indicates that this conversion from $BaCO_3$ to $Ba(NOx)_2$ reaches thermochemical equilibrium at this condition.

The difference of NOx dispersion in NSR catalyst without and with CO_2 was investigated. It was clarified that the NOx storage amount is equally reduced from catalyst upstream to downstream by the existence of CO_2 in the exhaust gas.