

TPR-XAFS study for water formation reaction of precious metal nanoparticle catalysts

D. Matsumura, T. Tsuji, Y. Nishihata (Japan Atomic Energy Agency), M. Taniguchi (Daihatsu Motor Co., Ltd.), H. Tanaka (Kwansei Gakuin University)

daiju@spring8.or.jp

Hydrogen gas management in nuclear power plants is very important for keeping safe operation. Some paths of hydrogen gas formation exist such as radiolytic decomposition of water molecules. In case of severe accident, hydrogen management system which needs external electric power will not work due to the shutdown of electric supplies. An alternative hydrogen management system which does not rely upon external electric power should be required. Hydrogen removal system with a catalyst, which utilizes water formation (hydrogen recombination) reaction between emerged hydrogen gas and oxygen gas in the air, is one of the candidates for hydrogen mitigation. Because this reaction itself is exothermic and passive one, it does not need external power supply. This system is called as passive autocatalytic recombiner (PAR) and greatly hoped to be developed.

Pd, Rh and Pt metal nanoparticle catalysts on Al₂O₃ and CeZrYO_x (CZY) supports are used for the study. In situ and time-resolved structure change of precious metal nanoparticle catalysts during water formation reaction was observed by using simultaneous measurement of temperature-programmed reaction and X-ray absorption fine structure (TPR-XAFS). Dispersive optics are expected to bring about high-precision data set of time-resolved XAFS spectra in real-time measurement because there are no mechanical motion components in the optics. We have observed XAFS spectra with dispersive optics at 2 Hz for Al₂O₃ support samples and 0.2 Hz for CZY support samples.

Carbon monoxide produced by the molten corium concrete interaction is considered as impediments for the safety management of PARs. In this study, a poisoning effect by carbon monoxide on catalytic activity was focused. We can distinguish the surface adsorption species of carbon monoxide and oxygen for Pt metal nanoparticles by monitoring the peak intensity and position of Pt L₃-edge XAFS spectra. TPR-XAFS for Pt(4 wt%)/Al₂O₃ catalyst were obtained with a flow of H₂(10%)+O₂(10%)+CO(1%). Sudden increase of carbon dioxide and water molecules, and sudden decrease of hydrogen is observed at around 110 °C. And at the same time and temperature, sweep increase of the peak intensity and sweep negative shift of the peak position were shown. This indicates that the adsorbed carbon monoxide was quickly decomposed and the surface of Pt metal nanoparticles was fast covered by oxide. In the case of CZY support sample, the continuous generation of water and carbon dioxide molecules were observed at room temperature. This means that the water formation reaction proceeds even at room temperature and under the existence of carbon monoxide. TPR-XAFS study for the catalyst revealed that the surface of Pt metal nanoparticles fast covered by surface oxide layer right after the mixture gas flows. It has been cleared that CZY support samples can work at room temperature as PAR against CO poisoning effect owing to the creation of surface oxide layer.

We have shown that catalytic activity is closely connected with the creation of surface oxide layer on some precious metal nanoparticles. We have overcome CO poisoning effect at room temperature for water formation reaction by using CZY as a support material.