

TEM Investigation on the Relationship Between Catalytic Activity and Structure in Rh/Al₂O₃ Catalysts

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Supported noble metal catalysts, such as Platinum (Pt), Palladium (Pd) and Rhodium (Rh), are widely used as three-way catalysts (TWCs) in automotive industry to reduce the emission of exhaust gases. In particular, Rh is the most favorable choice over Pt and Pd due to the activity of Rh under both lean (above stoichiometric air-fuel ratio) and rich (below stoichiometric air-fuel ratio) conditions in addition to a low production of undesired NH₃ [1]. However, Rh-based catalysts exhibit deactivation phenomenon at elevated temperatures due to strong interactions with the support, here alumina (Al₂O₃), for a variety of reasons [2-7], such as diffusion into supports [2, 3] and particle growth [4]. The ambiguity in understanding Rh deactivation at elevated temperatures is due to the lack of direct atomic-scale observation of the interaction between Rh metal particles and the oxide support surface. In this study, the effects of morphology changes of actual Rh/Al₂O₃ automotive catalysts and the metal-support interactions on the catalytic activity under alternating lean and rich conditions are investigated using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS).

Rh/Al₂O₃ (5wt%) catalysts were prepared using incipient wetness impregnation and were calcined at 600°C followed by reduction in H₂ environment at 450°C. Subsequent oxidation in O₂ environment above 900°C and further regeneration reduced in H₂ at 850°C were done to study the oxidation and regeneration effect in comparison with pulsator-aged catalysts. The activity of the catalysts was examined by light-off tests with a typical three-way catalyst feed mixture. Rh/Al₂O₃ powder was tested in a plug-flow reactor and the activity was determined based on the temperature at which 50% conversions of CO, C₃H₆, and NO is achieved. TEM specimens were prepared by crashing the treated catalysts powders and dispersing in ethanol and dropping onto a copper TEM grid with lacey carbon films. The high-resolution high-angle annular dark-field (HAADF) STEM images were carried out using a Titan 60-300 S/TEM. EEL spectra were collected using a Gatan Image Filter (GIF) Quantum ERS system with the energy resolution of 1 eV. The particle size distribution measurements have been carried out on at least 50 individual particles.

Figure 1a shows high-resolution STEM image of an individual Rh particle. Figure 1b&c show HAADF STEM images of freshly reduced catalyst with Rh-metal particles evenly distributed on the Al₂O₃ support with an average particle size of 1.6 nm ± 0.5 nm. After oxidation at 950°C, the catalyst is now composed of Rh atom clusters with an average size of 0.6 nm ± 0.2 nm (as indicated by arrows in Figure 1d) and sintered Rh particles with particle size of 12.5 nm ± 3.3 nm (Figure 1e). As shown in Figure 1f&g, further reduction at 850°C leads to the reappearance of the Rh particles with an average particle size of 1.7 nm ± 0.3 nm and the coexistence of larger coalesced Rh particles (22.1 nm ± 8.2 nm). In Figure 2, a series of EEL spectra taken across the sintered Rh particles shows the variation in the local chemistry. The Rh M₂ peak accompanying with the split of oxygen K edge suggests the change of local bonding environments of Rh as well as of oxygen. The split of O K edge is believed to be a pre-edge peak from a metal oxide exhibiting varying oxidation states. This indicates that, after treatment under oxidizing conditions, the Rh nanoparticles not only sinter into larger particles but also form rhodium oxide. Based on the temperature at which 50% conversion is achieved, the second reduction step at 850°C reverses the previously observed

catalysts deactivation and restores the activity. This ability to restore catalytic activity when used in an automotive catalytic converter application makes Rh-based catalysts more competitive compared to the established Pt- and Pd-based catalysts that are more susceptible to the sintering effect and thus the loss in catalytic activity in working conditions [8].

References:

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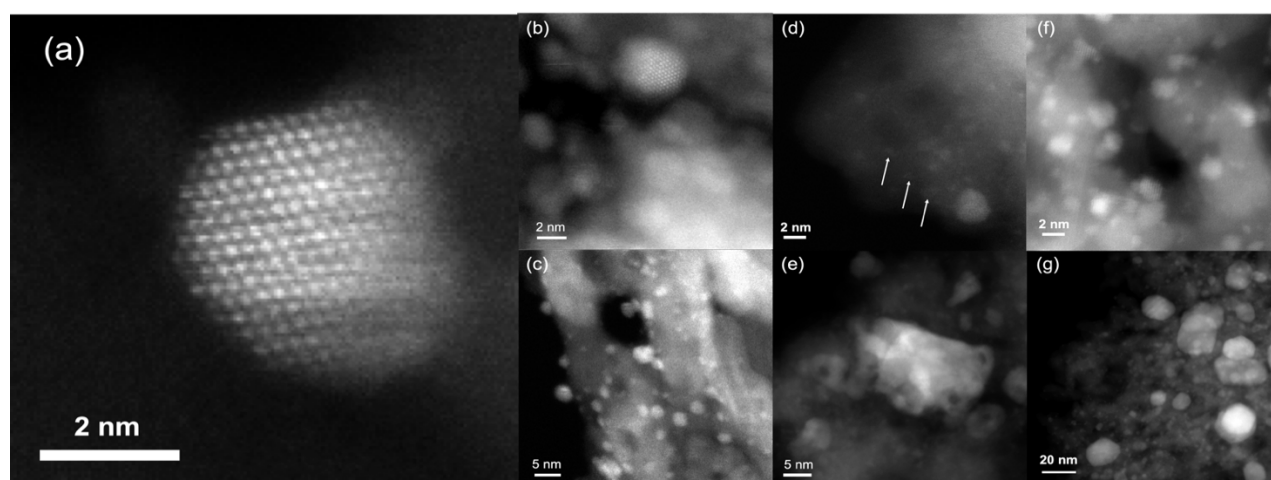


Figure 1. High-angle annular dark-field (HAADF) STEM images of 5 wt.% Rh/Al₂O₃. (a) high-resolution HAADF STEM image of Rh particle, (b, c) under reducing conditions at 450°C, (d, e) subsequent oxidation at 950 °C, and (f, g) reductive regeneration at 850 °C. The arrows in (d) indicate the Rh atom clusters embedded in the support.

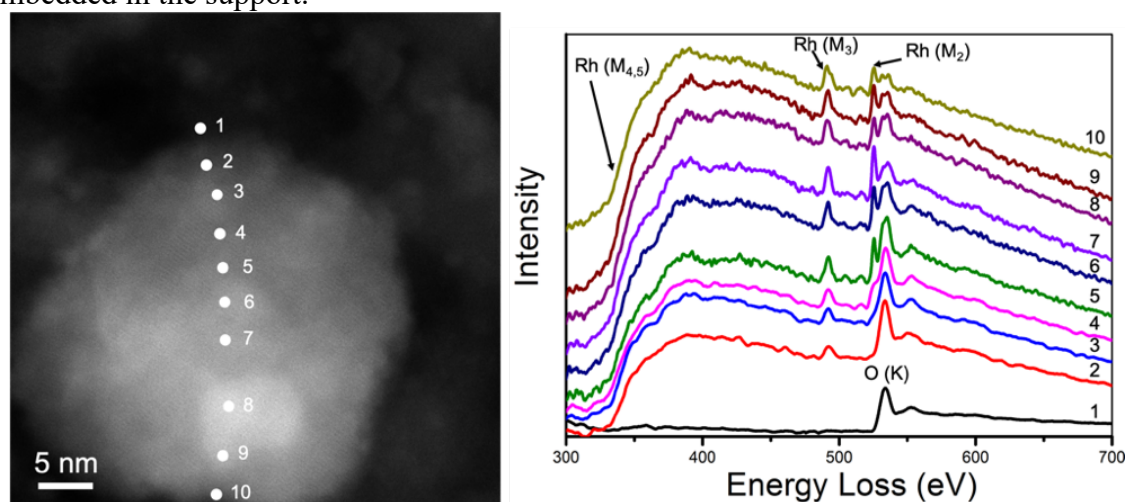


Figure 2. HAADF STEM image of oxidized Rh/Al₂O₃ catalysts with EEL spectra of the core structure in the region of 300 eV to 700 eV from ten individual positions across a sintered Rh particle.