

Direct Visualization of Spinel-Like Rhodium Aluminate (RhAlO_x) to Understand its Role in Rh/ Al_2O_3 -Based Three-Way Catalysts

Cheng-Han Li¹, Jason Wu² and Joerg R. Jinschek^{1,3,*}

¹ The Ohio State University, Department of Materials Science and Engineering, Columbus, OH, United States.

² Ford Motor Company, Dearborn, MI, United States.

³ Technical University of Denmark, DTU Nanolab, Kgs Lyngby, Denmark.

* Corresponding author: jojin@dtu.dk

Many long-debated scientific research questions remain ambiguous for decades due to the lack of direct visualization of the atomic structure in the material. Hence, fundamental mechanisms could only be partially revealed and understood due to limited information, e.g., provided by averaging and/or indirect characterization methods. With the advent of aberration-corrected scanning / transmission electron microscopy (STEM), direct atomic-resolution observation of complex material structures is now feasible [1].

Oxide-supported precious metal nanoparticle catalysts have been widely used for water-gas shift reactions, steam reforming, and exhaust gas conversion [2,3]. In the past decade, due to the increasing stringent regulations to exhaust emissions in fossil fuel-based vehicles and the shortage of raw material supply, it is imperative to enhance the efficiency of exhaust gas emissions by new design and formula of the environmental catalysts. Rhodium (Rh)-based catalysts, exhibiting the superior catalytic activity among noble metals, however, tend to deactivate under oxidizing conditions [4]. In the literature, such deactivation mechanism of alumina (Al_2O_3)-supported Rh-based catalysts has been attributed to the formation of inactive Rh oxides, migration of Rh into the Al_2O_3 support, and the formation of Rh aluminate (RhAlO_x), based on averaging method such as X-ray absorption spectroscopy (XAS), or indirect method such as temperature-programmed reduction (TPR) techniques [5].

Here, a systematic study of the deactivation and regeneration cycle in a Rh/ Al_2O_3 -based catalyst (see figure 1) under three-way catalyst (TWC) conditions has been performed, and the structure-property relationship on the atomic scale has been established [6]. Advanced aberration-corrected STEM and electron energy-loss spectroscopy (EELS) have enabled the direct visualization of Rh aluminate (RhAlO_x), to confirm its existence and to reveal its structure. In combination with activity (light off measurements) and EXAFS data, the formation of RhAlO_x can be attributed to the deactivation mechanism under high-temperature oxidizing conditions. RhAlO_x species exhibit a spinel-like structure, and by using high-resolution high-angle annular dark-field (HAADF) STEM imaging (figure 2), Rh atoms were found preferentially substituted into the (220) lattice plane of $\gamma\text{-Al}_2\text{O}_3$. And, using projections of cubic model of $\gamma\text{-Al}_2\text{O}_3$, HAADF-STEM intensities reveal that the Rh atoms preferentially occupy the octahedral sites in defected spinel $\gamma\text{-Al}_2\text{O}_3$. After subsequent reduction in H_2 (catalyst regeneration), 1–2 nm-sized Rh nanoparticles reappear at previous sites of RhAlO_x species, explaining the fully regained catalytic activity [6].

In summary, a long-debated deactivation mechanism Rh/ Al_2O_3 -based catalyst has been validated, by direct visualization of the formation of Rh alumina species using atomic-resolution HAADF-STEM imaging, in combination with activity measurements as well as EELS, XRD, EXAFS [7].

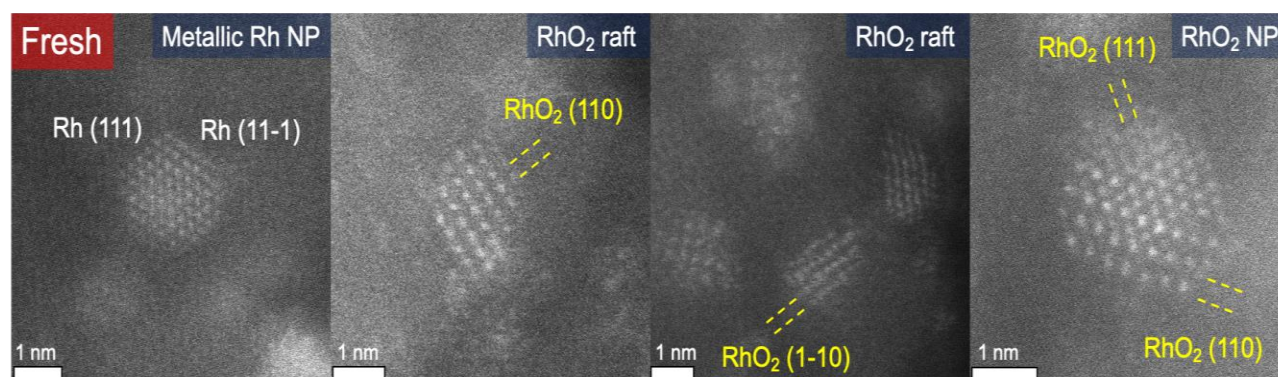


Fig. 1. HAADF-STEM images of fresh Rh/Al₂O₃ catalysts, showing the coexistence of metallic Rh nanoparticles, Rh oxide surface rafts, and RhO₂ nanoparticle. (Reprinted (adapted) with permission from [6]. Copyright 2022 American Chemical Society.)

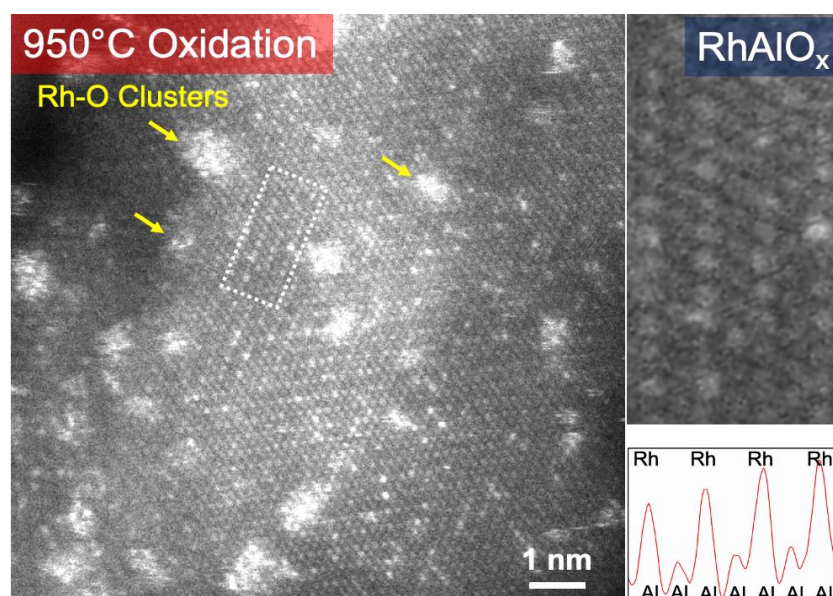


Fig. 2. HAADF-STEM images of Rh/Al₂O₃ catalysts after oxidation in air at 950°C, showing poorly crystalline Rh-O surface clusters and highly crystalline rhodium aluminate (RhAlO_x), identified by the regular incorporation of Rh atoms into one variant of (220) lattice planes of γ -Al₂O₃. High magnification image (top-right) of area in white dotted box and the corresponding integrated intensity line profile (bottom-right), highlighting the preferential occupancy of Rh in γ -Al₂O₃. (Reprinted (adapted) with permission from [6]. Copyright 2022 American Chemical Society.)

References:

- [1] P Batson, N Dellby and O Krivanek, *Nature* **418** (2002), p. 617.
doi.org/10.1038/nature00972
- [2] ED Park, D Lee and HC Lee, *Catalysis Today* **139** (2009), p. 280.
doi.org/10.1016/j.cattod.2008.06.027

[3] Y Zhai et al., *Science* **329** (2010), p. 1633. DOI: 10.1126/science.1192449

[4] M Shelef and GW Graham, *Catalysis Reviews* **36** (1994), p. 433, DOI: 10.1080/01614949408009468

[5] CP Hwang, CT Yeh and Q Zhu, *Catalysis Today* **51** (1999), p. 93, doi.org/10.1016/S0920-5861(99)00011-5.

[6] CH Li et al., *Chemistry of Materials* (2022), Article ASAP, doi.org/10.1021/acs.chemmater.1c03513

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