Aberration-corrected STEM imaging of Ag/Al_2O_3 Lean NO_x Catalyst

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Introduction

Active lean NO_x catalysts are an attractive strategy for treating NO_x emissions from lean burn gasoline and diesel engines. The Ag/Al_2O_3 system has been shown to exhibit good NO_x conversion over a narrow temperature range [1,2]. The morphology and surface properties of the Al_2O_3 have a major effect on the NO_x conversion efficiency [3]. Despite numerous studies, however, the nature of the active form of Ag is a subject of continued debate. We have investigated the nature of the active form of the Ag species on γ-Al_2O_3 via aberration-corrected [4] scanning transmission electron microscopy (STEM), which allows for the direct imaging of metal species down to single atoms on Al_2O_3 [5], in conjunction with *ex-situ* reactor studies [6]. High-angle annular dark-field (HA-ADF) images were recorded, then the sample was exposed to simulated lean diesel exhaust at relevant temperatures, and finally the same areas re-imaged to provide information on the nanostructural changes due to the *ex-situ* exposure.

Materials and Methods

The γ-Al_2O_3 was prepared according to the method disclosed in [3]. Ag was added at the 2 wt.% level by suspending the Al_2O_3 in an aqueous $AgNO_3$ (Aldrich) solution which was subsequently heated to 70°C with stirring to slowly evaporate the water. The resulting powder was pyrolyzed in an alumina crucible at 1°C/min to 450°C for 4h. Due to the light sensitivity of Ag, the powders were stored in light-tight containers and handled only under red safelight illumination. Powders were deposited onto a holey $LaCrO_3$-coated stainless steel grid. The nature of the Ag species as-deposited and following exposure to simulated lean diesel exhaust at various temperatures were characterized on a JEOL 2200FS equipped with a CEOS Co. hexapole probe corrector.

Results and Discussion

Initial images of the as-deposited Ag revealed a diverse collection of Ag species on the Al_2O_3. The majority of the Ag was in the form of individual atoms of Ag, but small clusters are also seen which were 2-3 atom layers thick, and had not yet formed a regular crystal. The ability of aberration-corrected STEM imaging to provide direct evidence of individual atoms of Ag on a high surface area Al_2O_3 substrate has thus been demonstrated. Following exposure to simulated diesel exhaust at 550°C for 2h, a small number of metallic Ag nanocrystals were observed to have formed, as seen in Fig. 1a. However, the majority of Ag species was still ultra-dispersed Ag atoms on the surface. Small clusters of Ag were also seen (Fig. 1b). An as-deposited specimen was also briefly exposed to light; the resulting microstructure is seen in Figure 2a. The nanoparticle that formed via photo reduction was 70 nm in diameter. After exposure at 450°C for 1h, the Ag nanoparticle had re-dispersed as shown in Figure 2b. The state of Ag on alumina under lean diesel exhaust conditions is therefore seen to be a complicated mixture of single Ag atoms, small two-dimensional clusters and nanoparticles. Larger photo-reduced metallic Ag particles reduce quickly at low temperatures in the lean diesel exhaust environment.

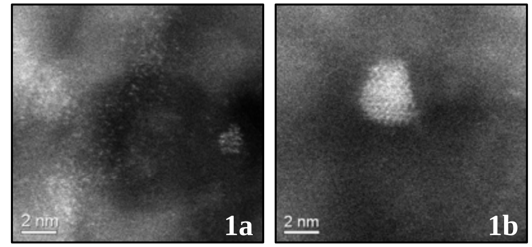

Figure 1. As-deposited Ag/Al_2O_3. a,b) Single Ag atoms and small clusters of Ag are evident.

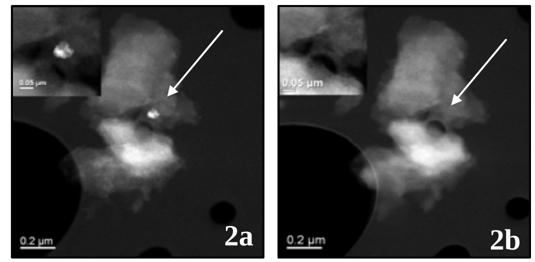

Figure 2. a) As-deposited Ag/Al_2O_3 following light exposure. 70 nm Ag nanoparticle seen.
b) After 1 hour at 450°C in simulated diesel exhaust, the 70 nm Ag particle has re-dispersed.

Significance

Aberration-corrected STEM imaging is capable of imaging individual atoms of Ag on γ-Al_2O_3. After exposure to simulated lean diesel exhaust at 450-550°C, the predominant species is Ag atoms, with some small clusters and a small number of nanocrystals. Large (10s of nm), photo-reduced Ag particles formed quickly at room temperature, but upon exposure at 450°C for 1 hour in lean diesel exhaust simulant, the nanoparticles re-dispersed.

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