

Understanding the Effect of Halide Poisoning in CO oxidation over Au/TiO₂

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Introduction

Nanosized Au particles are well known for their ability to catalyze carbon monoxide oxidation at low temperatures on a variety of supports [1,2]. However, these catalysts are typically prepared from chloroauric acid, and the residual chloride suppresses the activity. Although it has been shown that residual chloride causes agglomeration of Au particles, there is evidence that the effect is present even when the Au particle size remains unchanged. Recently, we have shown that, similar to chloride, bromide also poisons these catalysts. Since the poisoning involves the active sites directly, it can be used as a tool to interrogate the active sites. Earlier we demonstrated that we could follow the development of catalytic activity by in-situ spectroscopies [3]. Thus, it is possible to delineate the effect of halide on the oxidized and the reduced form of the catalyst. Here, we report the results of an investigation of the effect of bromide on Au/TiO₂ catalysts both before and after the catalyst has been reduced using a combination of in-situ FTIR spectroscopy, X-ray absorption spectroscopy, and microreactor studies.

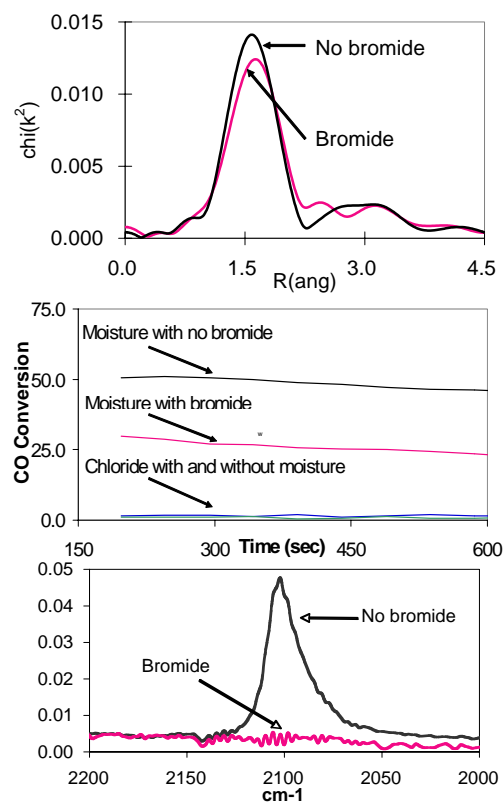
Materials and Methods

Au/TiO₂ catalyst was prepared by deposition precipitation using HAuCl₄ (Aldrich, 99.999%) as the precursor and microrutile as the support (Sachtleben, 65m² g⁻¹). A .007M HAuCl₄ solution was stirred vigorously at pH 7 (adjusted with NaOH) for 1 hour at 70°C, then slowly added to a suspension of TiO₂ while maintaining pH 7. The resulting suspension was stirred at 40°C for 2 hours. The solid was suction-filtered and washed repeatedly with deionized distilled water to remove residual chloride, then dried at room temperature in air.

FTIR data were collected in a Nicolet 670 FTIR spectrometer with a MCT detector. The IR cell was a 6cm³ stainless steel cylinder with CaF₂ windows. The catalyst was loaded as a self-supporting wafer. Spectra were obtained in transmission mode with 15 s acquisition time and 4 cm⁻¹ resolution. XAS experiments were conducted at the beamline 5-BMD of the DND-CAT at the Advanced Photon Source at Argonne National Laboratory using methods described previously [4]. Catalytic data were collected by analyzing exit gases with gas chromatography.

Results and Discussion

As prepared, Au is present entirely as Au³⁺. Addition of small amounts of bromide to the as-prepared sample suppresses the catalytic activity noticeably. For samples not containing bromide, XANES shows that the catalyst is fully reduced to metallic gold after exposure to the reaction mixture for CO oxidation. However, if the sample contains bromide, some Au cations remain. EXAFS shows the presence of Au-Br scattering and a decrease in



Au-O scattering, suggesting that Br replaces some O (or (OH)) ligands, preventing the Au cations from being reduced and forming active sites (Fig. 1A). Addition of Br to a reduced sample also suppresses the catalytic activity significantly (Fig. 1B). On this sample, XANES did not detect evidence of re-oxidation, implying no corrosive adsorption of bromide. However, the IR intensity of adsorbed CO is significantly suppressed, suggesting that Br poisoning is due to physical blocking of the active sites on metallic Au (Fig. 1C). Moisture increases the mobility of bromide, which is reflected by more severe activity losses.

Significance

Bromide suppresses the activity for CO oxidation by different mechanisms on an unactivated (oxidized) and an activated (reduced) Au/TiO₂. The data are consistent with the active sites being metallic Au.

Figure 1. (A) Change in Au-O and Au-Br scattering upon addition of bromide to unreduced Au/TiO₂. (B) Effect of halide and moisture on catalytic activity of reduced Au/TiO₂. (C) Change in IR absorption bands resulting from addition of bromide to reduced Au/TiO₂.

References

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